EFFECTS OF DEHYDRATION ON PHYSICO-CHEMICAL PROPERTIES OF SELECTED VOLCANIC ASH SOILS FROM HAWAII

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INTRODUCTION

No soil can continuously sustain a constant moisture content. Instead, regardless of amount of rainfall, all soils, in upland or paddy positions, in temperate or tropical areas, experience various drying and wetting cycles by natural or artificial means. In Hawaii, it may be presumed that moisture regimes are so widely different that moisture content fluctuations in surface soils may range between saturation and completely sun-dried conditions. Exceptions to this are the uncultivated forest soils such as certain Typic Hydrandepts, which always remain moist due to large amounts of rainfall and to being continually heavily covered with vegetation. When exposed for cropping or other uses, such soils can undergo drying for the first time in their history. Subsequently, changes in soil behavior may then occur, which sometimes present problems such as changes in soil susceptibility to erosion.

Drying and wetting cycles are known to have significant effects on physico-chemical and perhaps mineralogical properties of soils. This is particularly true for soils in which noncrystalline components are important constituents because of the highly reactive and sensitive physico-chemical behavior of these constituents. Many Hawaiian soils contain various amounts of such noncrystalline colloidal constituents, as revealed by the lack

of or very weak x-ray diffraction maxima. These may be gel-like silicates, hydrated oxides of aluminum and iron, and/or organic matter (Chan, 1972). Knowing their properties is important for the understanding of physical, chemical, and physico-chemical behavior of soils and for predicting possible consequences of management factors, including effects of drying and wetting.

Theoretically, dehydration of a soil may involve reductions of water content from saturation to field moisture capacity (pF about 1.5 - 2.5 or 0.0316 - 0.316 bar), to ion-hydration or surface adsorbed water (hygroscopic water: pF about 4.5 = 31 bar), to structural water when sufficient dehydration energy is used. El-Swaify and Henderson (1967) divided water in this region into the following categories in order of increasing energy of removal:

$$\psi_m = \psi_{mi} + \psi_{mc} + \psi_{mh} + \psi_{ms} \qquad (1)$$

where the left hand term represents all the water held by matric forces, and the right hand terms represent the water retained due to interacting diffuse double layer (swelling), capillarity, ion or surface hydration, and water incorporated within mineral structure, respectively. The drying process also involves a sequential change in the nature of interparticle forces and subsequent interactions. First, with abundant water present, interparticle linkages are caused mainly by mutual hydrogen bonds

involving water molecules. Second, certain direct interparticle attractions are caused by electrostatic and hydrogen bonds (El-Swaify and Emerson, 1975). Third, when interparticle separations are sufficiently small, attractions may be caused by van der Waal's forces. All these attractive energy components increase in magnitude with decreasing interparticle distance. Therefore, it may be expected that closer contact between particles as is achieved by drying to near or beyond the adsorbed water ranges, i.e., beyond a film thickness of one or two molecular layers of water or around 10Å thickness (van Olphen, 1963), enhances stronger interparticle attractions. Finally, when adsorbed water is completely removed, particles may be more strongly attracted by van der Waal's attraction in addition to the above attraction forces. When dried beyond this point, particles begin to lose structural water, possibly giving rise to mineralogical changes.

Little information is available on mechanisms of water retention by and effects of dehydration on Hawaii's Typic Hydrandepts. Except for El-Swaify and Lim (1976), most dehydration studies were performed under undefined conditions such as air-drying or sun-drying (e.g., Kanehiro and Sherman, 1956). Similarly, limited effort was made to investigate the roles of various soil constituents in the drying process and to determine the extent to which soil properties may be restored by rehydration.

The main objectives of the present research were to:

A. Investigate the effects of well-defined dehydration treatments on the physico-chemical properties of selected volcanic ash soils.

B. Employ synthetic and selective extraction techniques to verify the roles of various constituents in effecting changes in soil properties as a result of drying.

C. Investigate the extent to which original soil properties may be restored to dried soils by various rehydration treatments.

LITERATURE REVIEW

A. Theory and Concepts of Soil Water

Since dehydration of soils involves removal of water by either evaporation or drainage, and since soil water is important not only from physical but also chemical, mineralogical, and nutritional standpoints, it is important to start this section with a brief discussion of the theory and concepts of soil water.

Historically, two slightly different views of soil water gave rise to present concepts of soil water. Briggs (1897) tried to develop a concept for the mechanics of soil moisture primarily based on the so-called capillary tube hypothesis. He conceived that capillary water exists as a continuous and tightly stretched film around soil particles and visualized the forces arising from the curvature of these capillary water surfaces as the principal cause of the retention of soil moisture. Accordingly, water movement would be expected to take place from thicker to thinner films with the rates of movement being related to differences in film curvature, the surface tension, and the viscosity of the liquid. Consequently, he proposed classification of soil water into three categories:

1. Hygroscopic water, which is absorbed from an atmosphere of water vapor as a result of attractive forces at the surfaces of soil particles.

2. Capillary water, which is held by surface tension forces as continuous films around the particles and in capillary spaces.
3. Gravitational water, which is not held by the soil but drains under the influence of gravity.

Later, Briggs and McLane (1907), using centrifuge equipment, developed the moisture equivalent as an expression of soil ability to hold water under a centrifugal force 1000 times that of gravity. Bouyoucos (1921, 1936) criticized the above classification and suggested a new classification of soil water on the basis of results obtained from freezing-point and dialatometer studies. His proposed classification of soil water was as follows:

1. Gravitational, which is superavailable to plants.
2. Free, which is available to plants.
3. Unfree: a. Capillary-absorbed, which is only slightly available to plants.
   b. Combined, including both the water of solid solution and water of hydration, neither of which is available to plants.

Gravitational water needs no explanation. Free water is that which freezes for the first time due to supercooling at -1.5°C. Capillary-absorbed water is that which freezes last due to supercooling at -4°C and at -78°C minus the free water. Combined water is that which does not freeze at all.

Buckingham, in 1907, explained soil moisture retention in terms of energy which is acting between soil and water introducing the term "capillary potential." Characterized by letter ψ, this term expresses the value which measures the attraction of soil for water at any given point. Gardner (1920a, 1920b) expanded Buckingham's idea, pointing out that the capillary potential is a linear function of the reciprocal of moisture content over a considerable range of the curve relating the two according to the equation:

$$\psi = (e/\theta) + b \qquad (2)$$

In equation (2), ψ is the capillary potential, θ is the moisture content, and e and b are constants. The equation indicates that the potential moisture curve is hyperbolic in nature. Russell and Richards (1938) determined capillary potential by a centrifugation method applying relation:

$$\frac{d\psi}{dr} = r\omega^2 \qquad (3)$$

where r and ω are the radius of centrifuge and angular velocity, respectively. By holding ω constant, equation (3) was integrated between the limits of r_1 and r_2 to obtain:

$$\psi_1 - \psi_2 = \frac{\omega^2}{2}(r_1^2 - r_2^2) \qquad (4)$$

In applying the centrifuge method, r_1 represents the radial

distance from center of rotation to the free water surface, r_2 the distance to the soil, and ψ_1 the capillary potential at distance r_1. Since it is customary to choose free water surface as a reference level, $\psi_1 = 0$ at that point. Therefore, ψ_2, the capillary potential of water in the soil, becomes:

$$\psi_2 = \frac{\omega^2}{2}(r^2_2 - r^2_1) \quad (5)$$

They found that pF 4.2 was in good agreement with experimentally determined wilting points by equation (5).

Recently, Baver (1972) theoretically defined the total potential for water present in any soil system as:

$$\psi_T = \psi_m + \psi_g + \psi_p + \psi_\pi + \psi_\Omega \quad (6)$$

where ψ_m, ψ_g, ψ_p, ψ_π, and ψ_Ω are the matric, gravity, pressure, osmotic, and overburden potentials, respectively.

El-Swaify and Henderson (1967), in their studies of water retention by colloidal clays, further subdivided the matric component into four categories in order of increasing energy of removal. Those categories, expressed in equation (1), represent the water retained due to expansion caused by interacting diffuse double layers (swelling), capillarity, ionic or surface hydration, and water incorporated within mineral structures, respectively. The first three categories are expected to prevail at ordinary temperatures. However, the last term which

determines the possible occurrence of mineralogical transformations is generally associated with such high energies that losses of structural water are expected only at elevated temperatures. For Hawaii's Typic Hydrandepts, El-Swaify and Lim (1976) argued that even long-term dehydration at ordinary temperatures is not theoretically expected to cause crystallization of amorphous $Al(OH)_3$ to gibbsite. Rather, the gibbsite detected in such soils, even after drying in the laboratory, is an actual natural constituent of the soils.

B. Colloidal Particle Interactions

A most obvious implication of dehydration is the change in the nature of interparticle forces and subsequent interactions among soil particles. The theory of colloidal stability which was developed by Derjaguin and Landau (1941) and by Verwey and Overbeek (1948), is applicable to the dehydration process. This, henceforth called the DLVO theory, describes the interactions between colloidal particles in terms of repulsive forces, which find their origin in the electrochemical double layer and attractive forces of the van der Waal's-London type. The transition from a stable to a flocculated system can be represented by the net interaction energy of these two energy components.

1. Repulsion energy (V_R)

Repulsion between similarly charged particles takes place

because of their formed diffuse double layers (Gouy, 1910 and 1917 and Chapman, 1913). The repulsive energy is the amount of work required to bring the particles from an infinitely large distance of separation to a definite distance. Verwey and Overbeek (1948) have shown that the following approximate equation describes this repulsive energy, V_R, when the interaction between two plane-parallel surfaces is small:

$$V_R = \frac{64\ nkT}{\kappa} r^2 \exp(-2\kappa d) \qquad (7)$$

where d is the distance halfway between the plates, n is ion concentration and κ is defined by equation (10), k and T have their usual meanings, and

$$r = \frac{\exp(Ze\ \psi_o/2KT) - 1}{\exp(Ze\ \psi_o/2KT) + 1} \qquad (8)$$

in which Z represents the counter ion valency and ψ_o the potential at the particle surface. In general, however, the repulsive energy may be expressed by

$$V_R = \frac{N}{\kappa} f\ (\psi_o,\ \psi_d) = \frac{\kappa}{Z^2} f\ (\psi_o,\ \psi_d) \qquad (9)$$

where ψ_d is the electrical potential halfway between the particles, and

$$\kappa = \left(\frac{8\pi Z^2 e^2 n_o}{DkT}\right)^{\frac{1}{2}} \qquad (10)$$

Therefore, for a given value of ψ_o and ψ_d the V_R depends on the valency (Z) and concentration (n^o) of the electrolyte in the system. The value of V_R depends on ψ_o (since for a given distance between the particles ψ_d is a function of ψ_o) for a given value of κ and Z.

2. Attraction energy (V_A)

The attraction energy (V_A) between particles is mainly due to the van der Waal's attractions. Since van der Waal's attractions between atom pairs are additive, the total attraction between particles containing a large number of atoms is equal to the sum of all the attraction forces between every atom of both particles. The attraction energy derived by Verwey and Overbeek (1948) for a 2:1 clay is

$$V_A = -\frac{A}{48\pi}\left(\frac{1}{d^2} + \frac{1}{(d+\delta)^2} - \frac{2}{(d+\delta/2)^2}\right) \qquad (11)$$

where A is the van der Waal's-London constant which has a value of approximately 10^{-12} erg, δ is the thickness of interacting plates, and d is the halfway distance between two particles, respectively. This attraction energy decays with the second negative power of the distance thus having longer effective range than interatomic or intermolecular attractive energy which decays with the sixth negative power.

3. Total energy of interaction (V_T)

Based on the DLVO theory, van Olphen (1963) illustrated the applicability of the total energy of interaction to colloidal clay systems. Figure 1 is a schematic presentation of the repulsive and attractive energy for a given colloidal system as a function of particle separation at three electrolyte concentrations. As predicted by equation (11), the attraction component remains practically the same when electrolyte concentration in the medium is varied. On the contrary, double-layer repulsion decreases at higher electrolyte concentration. This was predicted by equations (7) and (10). Figures 2 (a), (b), and (c) illustrate the net interaction curves and subsequent soil colloidal stability. Figure 2 (c) shows no net repulsion at any interparticle distance at the high electrolyte concentration. It is expected, therefore, that particle agglomeration occurs in this system at a maximum rate, a process which is called "rapid coagulation." At intermediate electrolyte concentrations (Figure 2 (b)) the coagulation process is retarded by a small long-range net repulsion. Under this condition, "slow coagulation" takes place. At very low electrolyte concentrations (Figure 2 (a)), the coagulation process is retarded by the appreciable long-range net repulsion to such an extent that it may take the longest period of time for coagulation to become perceptible. Indeed, for all purposes, the sol remains stable under these conditions. From these net potential curves,

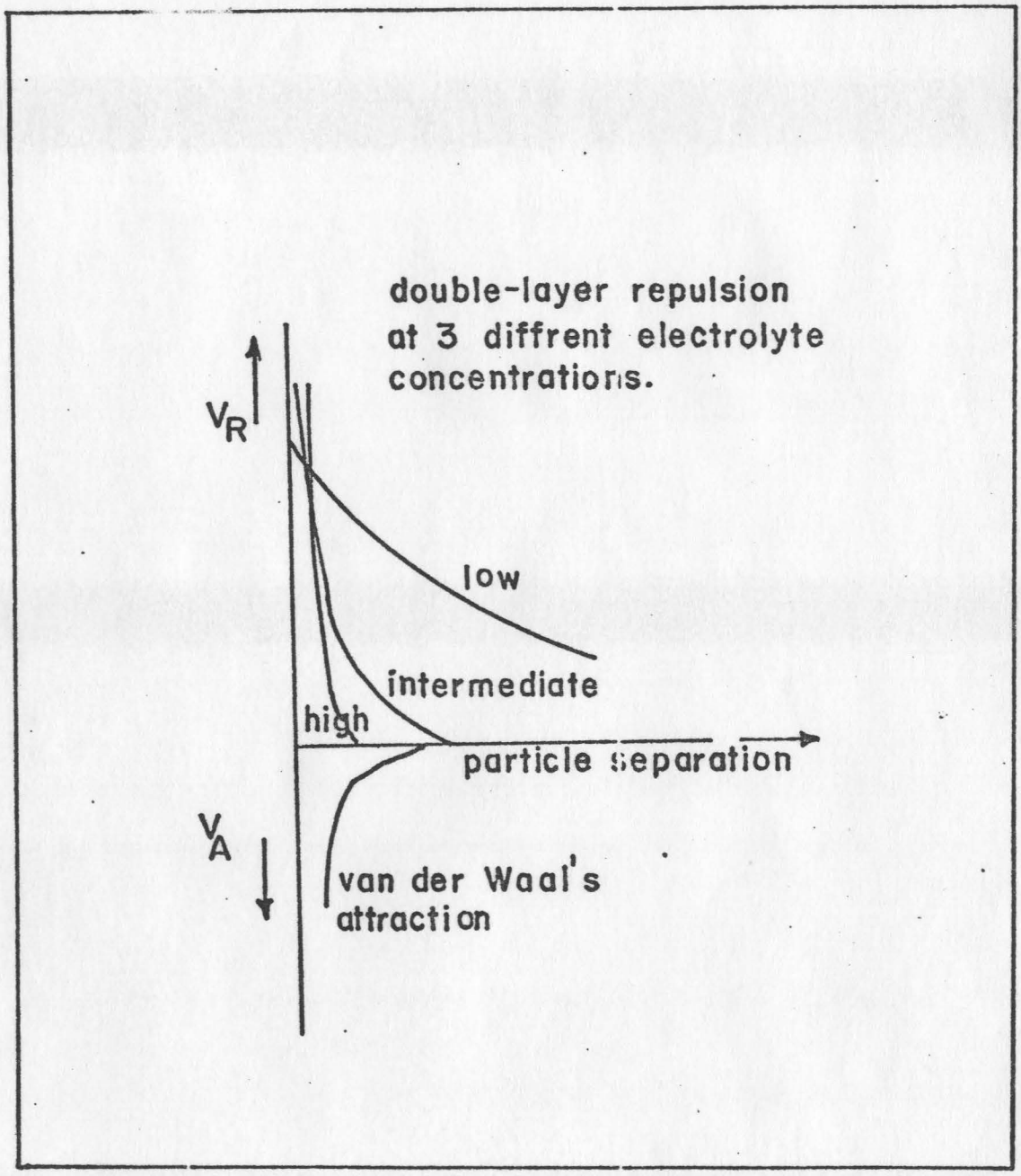

Figure 1. Repulsive and attractive energy as a function of particle separation at three electrolyte concentrations.

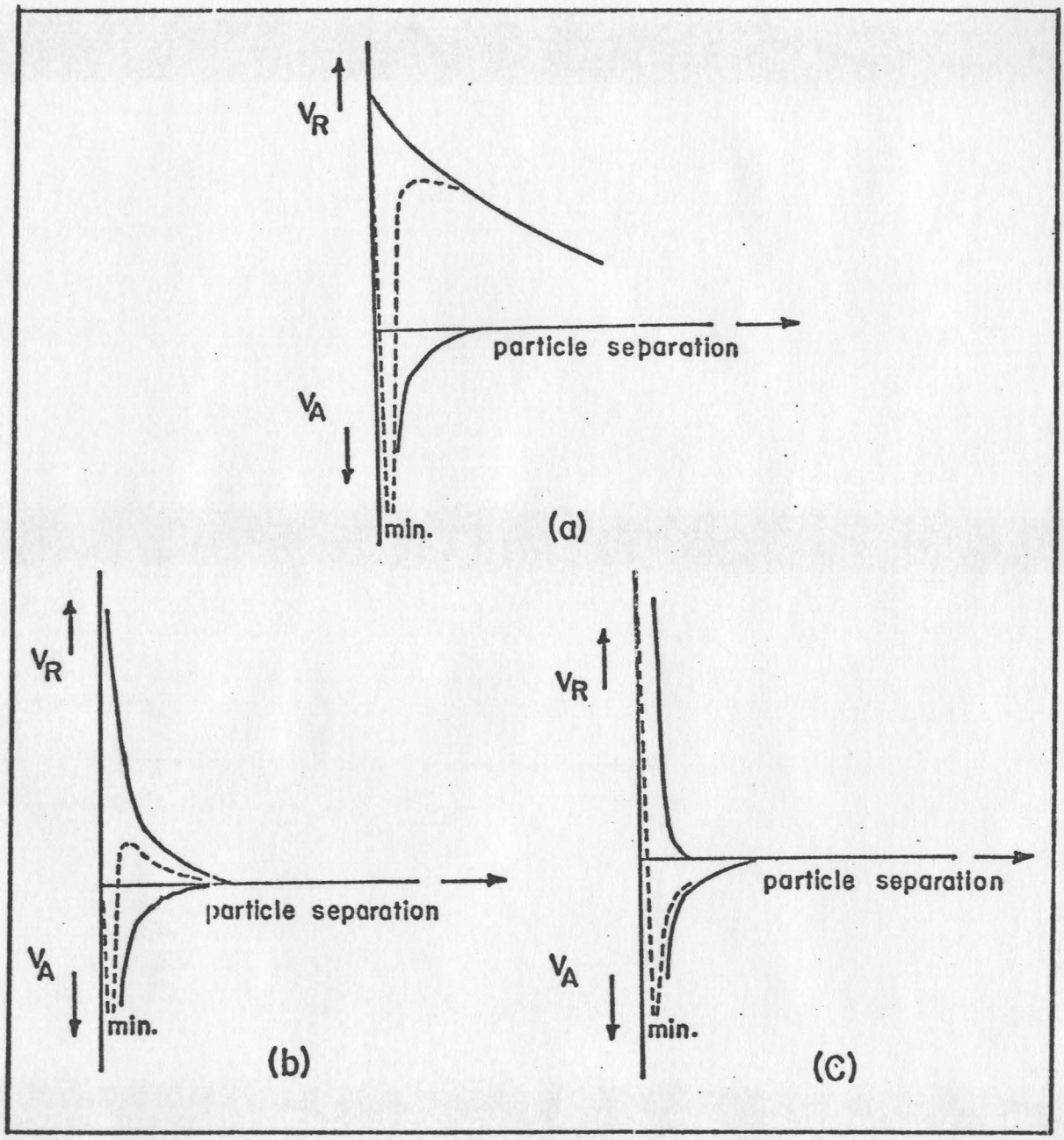

Figure 2. Net interaction energy as a function of particle separation.

(a) Low electrolyte concentration
(b) Intermediate electrolyte concentration
(c) High electrolyte concentration

it is clear that colloidal stability or flocculation for a given sol is primarily governed by interparticle distances and the degree of compression of the double layer by added electrolytes.

The dependence of net interaction energy on interparticle separation may be applied to the dehydration process. As water is lost from colloidal dispersions, suspended particles gradually get closer together until sufficient interparticle contacts prevent closer approach. Further drying beyond this point (the shrinkage limit) results in decreasing water film thickness around the particles. The relative net attraction energy between colloidal particles is determined by the average interparticle distances in the dried system. Subsequently, the degree of stability of aggregates or agglomerates in this system is affected by the attained degree of dehydration.

C. Effects of Dehydration Treatments on Physico-Chemical Properties of Soils

Powers (1932), working on peat soils, reported that the cation exchange capacity of lignin and hemicellulose fractions were reduced by drying. Sherman et al. (1953) observed that dehydration of colloidal hydrated oxides of the soil may be responsible for the development of indurated laterite horizons. They also reported that dehydration caused changes in compaction, bulk density, particle density, and particle size. Fieldes et al.

(1952) have shown, through artificially prepared amorphous hydrous oxides of Al, Ti, Fe, and Si that these oxides have high C.E.C., especially Al and Ti. But, crystalline forms of these oxides have low capacities. Consequently, they concluded that the C.E.C. of soils from the Lower Cook Islands Group was due mainly to amorphous colloidal hydrous oxides in them. Kanehiro and Sherman (1956) reported that C.E.C. of some Hawaiian soils were reduced upon drying. These reductions were most notable for the Hydrol Humic Latosols (now Typic Hydrandepts) and least notable for soils that undergo natural intense drying cycles. For the soils in this study, the reductions were 20-30% and 28-36% for Hilo soil, 42-66% and 55-75% for Akaka soil, upon oven-drying and sun-drying for 100 days in a glass house, respectively. Upon rehydration, these reductions were regained in the order of wet area soil<moderate wet area soil<dry area soil. Thus, very little reversibility was noted in the reduced C.E.C. of Typic Hydrandepts. Brown (1953) found that the amounts of cation exchanged into a resin from soils increased sharply as the soil moisture content increased through the range from wilting percentage to saturation. Reduction increments were much higher in the range between moisture equivalent and maximum water capacity. He explained this phenomenon, in addition to the factors of solubility, cation hydration, osmotic pressure, and changes in the equilibrium between

exchangeable cations and water soluble salts in soils (Kelly, 1948 and Reitemeier, 1946), by the larger thicknesses and continuity of water films within the pore systems of wet soils. With the entire pore system filled with water (at saturation), the thickness and continuity of water films allowed a hydrogen membrane (resin) in contact with the soil aggregates to maintain an efficient exchange of hydrogen ions for the cations held by the soil aggregates in immediate contact with it. At the same time, this film thickness permits the membrane to continue to absorb cations even after this soil surface, in contact with it, has been largely depleted of exchangeable cations, and also permit maximum exchange of cations demanded by the equilibria conditions existing within and between the soils and the membrane. Rana and Sherman (1971) reported nonimproved productivity and decreased P-fixation capacity of Akaka and Puhi soils upon drying at room temperature in the shade from moisture content at 260% to 80%, and 66% to 22%, respectively. Kadrekar and Kibe (1973) showed that alternate wetting after a drying treatment released more applied K faster from soils than continuously moist conditions. Also, air dried and oven dried soil released early and maximum amounts of K from nonexchangeable form in soils, respectively. Ahmad and Davis (1971) and Summerfield and Rieley (1973) reported similar results through their own experiments. Sorensen (1974) observed that the rate of organic

matter decomposition in soils increased by alternate air drying and wetting followed by incubation at 20°C. Bisal and Pelton (1971) showed that the integral heat of immersion of oven dried and freeze dried soils were equally higher than that for air dried soil. But, he pointed out the possibility that the freeze drying treatment caused an increase in surface area of the sample. Its effect on the heat of immersion was counterbalanced by the small amount of moisture which was retained as compared with that in the oven dried samples.

D. Synthetic and Selective Extraction Techniques to Verify the Roles of Various Constituents in Effecting Changes in Soil Properties as a Result of Drying

There is no doubt that precise understanding of the effects of individual soil components would help in any effective interpretation of the overall behavior of the rather complex and heterogeneous soil system. This idea is generally carried out by the synthetic and selective extraction techniques, yet neither technique is completely satisfactory. Results obtained by the former are difficult to interpret exactly because the synthetic minerals are not necessarily identical with the minerals occurring in natural soils (El-Swaify and Emerson, 1975). The latter technique raises considerable questions of validity because the extraction process is never really selective for a given soil constituent. Of the two

alternatives, however, the synthetic method raises less questions of validity.

Lutz (1938) attempted to investigate the effect of Fe on soil physico-chemical properties, precipitating Fe-hydroxides in electrodialized bentonite. Gastuche (1964) as well as Greenland and Oades (1968) have shown the possibility of successful synthesis of not only pure octahedral hydroxides, but also specific Al hydroxides and Fe(III)-hydrous oxides in the presence of silica. El-Rayah and Rowell (1973) precipitated Fe-hydrous oxides and Al-hydroxides into dispersed clay, clay aggregates, and orientated flakes of Na saturated Wyoming Bentonite. They concluded that Fe and Al interlayers reduced the swelling of Na-montmorillonite in NaCl solution. They noted that a deposit of sesquioxide around an aggregate or orientated flake of clay restricts swelling until the sesquioxide coating is broken by the swelling pressure of the clay, and that Al was a more effective suppressor of swelling than Fe. Blackmore (1973) illustrated that aggregates produced by mixing of clay with separately formed Fe(III)-precipitates were less stable than those produced when the clay was present during earlier stages of the precipitation reaction. Cornell et al. (1974) obtained the kinetic curve for the early stage of dissolution of synthetic goethite with 0.5N-HCl. They concluded that some amorphous ferric hydroxides exist, possibly as exterior coatings and dissolve very rapidly.

These usually did not represent more than 0.2% of the total mass of goethite. They further mentioned that the amount of amorphous material was not related to surface area alone but depended upon the precise conditions prevailing during the final stages of goethite crystallization. They did establish these conditions precisely. El-Swaify and Emerson (1975) and El-Swaify (1976) precipitated Fe- and Al-hydroxides in absence and in presence of clays. They observed that precipitated Fe consisted of particles about 40Å in diameter and amorphous in x-ray rather than the acicular goethite that precipitated under similar conditions in the absence of clay. Al was present as thin layers on the surface of clay particles and their form was generally indeterminate in contrast to the crystallized gibbsite or bayerite formed in the absence of clay. El-Swaify (1976), through observations of colloidal stability diagrams of hydroxide-treated clays as well as pure hydroxides, concluded that the colloidal stability of undried mixtures was dependent on the charge balance between individual constituents. It was also revealed that, after one drying cycle, all hydroxy treatments inhibited the double layer swelling of Na-clays in dilute NaCl solutions, that Al was more effective than Fe in reducing slaking of dry clay discs, and in increasing the resistance of clay to dispersion in phyrophosphate solutions.

In an attempt to improve selective extraction techniques, Tweneboah et al. (1969) proposed the 0.5M $CaCl_2$ at pH 1.5

solution for effective selective extraction of active Al from acid soils. After measuring changes in charge characteristics of soils before and after extraction, they suggested that the positive charges in the soils studied were mostly due to the "active" Al oxides. Their soils included several highly oxidic samples with one Oxisol (Krasnozem). Chan (1972) applied this extractant to the Hilo soil and showed that peak intensity in x-ray diffraction analysis was improved, and that the "gel-hull" surrounding clay particles was effectively removed by this extractant. Since Galabutskaya and Govorva (1934) in Russia removed Fe oxides from kaolin by reduction with sodium hydrosulphite, the technique received the attention of many workers. Deb (1950) modified this method and compared it with the oxalate-sunlight method. He concluded that neither method was quite satisfactory for removing free Fe oxides without affecting crystal structure, but the sodium hydrosulphite method proved superior. Aguilera and Jackson (1953), and later Mehra and Jackson (1958), again modified this method to sodium dithionite-citrate and then included a sodium bicarbonate buffer. They reported that this method was most effective in removal of free Fe oxides from latosolic soils and least destructive of silicate clays as indicated by least loss of C.E.C. after oxide removal.

Ammonium oxalate extraction was proposed by Tamm (1922) for Al, Fe, and Si extraction. Lundblad (1934) showed that this

reagent was useful in differentiating between certain classes of soils. Schwertmann (1964) retested this acidified ammonium oxalate as an extractant of Fe-oxides and found that it dissolved only x-ray amorphous oxides in darkness. Deb (1950), Gorbuner et al. (1961), and Mitchell (1964) observed that the dithionite method usually does not distinguish between hydrated Fe -oxides weathering products and crystalline primary Fe-oxides. Also, McKeague and Day (1966) determined Fe and Al extracted in acidified ammonium oxalate and bicarbonate buffered dithionite citrate extractants as aids in differentiating various classes of soils. They found that the ammonium oxalate contained more Fe and Al from amorphous materials than from crystalline oxides whereas the dithionite dissolved a large proportion of both crystalline and amorphous materials. Soils subjected to both extractions, however, gave much more clearly defined x-ray diffraction patterns than unextracted samples. Consequently, they concluded that both oxalate- and dithionite-extractable Fe and Al values are useful in studies of soil genesis and classifications because oxalate and dithionite values give an approximation of accumulation of amorphous products of recent weathering and of combined content of amorphous and crystalline forms of Fe oxides. In contrast, Arshad et al. (1972) reported that characterization of pedogenic horizons based on oxalate- and dithionite-extractable Fe and Al, might have limitations. Pawluk (1972)

reported that the double extraction with acidified ammonium oxalate and single extraction with dithionite extraction probably serve as good indications of relative amounts of amorphous and total "free" Fe oxides, respectively. He also reported that acidified ammonium oxalate removed more Fe than dithionite from both clay and very fine sand plus coarse silt fractions of soils but at a much slower rate. Schwertmann (1973) insisted that oxalate would not dissolve a major part of the crystalline Fe oxides in most soils based on evidence he obtained with synthetic lepidocrocites and goethites.

E. Restoration of Original Soil Properties After Dehydration

Puri and Keen (1925) tested how moisture content of the soil and the shaking period affect the degree of dispersion with soil moisture contents of 22.60%, 17.75%, and 3.62%, respectively. They illustrated drying effects on cementation were reached long before the air-dried state and that shaking was not necessarily enough to break down the aggregates. Warkentin and Maeda (1974) measured the shrinkage and plasticity characteristics of allophane soils from the West Indies and Japan in both moist and dried states. They reported that shrinkage and plasticity are the most unusual properties of allophane and that both change markedly upon drying in the following order of severity: oven drying> air drying>freeze drying. They further suggested that the

plasticity characteristics of allophane, namely a high liquid limit, low plastic index, and a decreased plasticity index on drying could be a basis for rating amount and nature of allophane in soils. Sherman et al. (1964) showed that drying of Typic Hydrandepts resulted in significant changes in many physico-chemical properties. When drying proceeded below a certain point, yet undefined, such changes were not reversible upon re-wetting. Since natural behavior of such soil is markedly influenced by abundant presence of x-ray amorphous colloidal constituents, they presumed that the drying process, even at ordinary room temperature, enhanced transformation of these constituents into crystalline minerals. Since Clelland, Cumming, and Ritchie (1952) reported "high solubility layer" on the surface of dust particles from a "rock crystal," workers tried to measure the thickness of such amorphous coating and whether they play a role in the stability of soil aggregates. For instance, Engelhardt (1955) estimated the thickness of the amorphous coatings to be 1-10Å. Using an electron microscope, Jones and Uehara (1973) observed amorphous gel coatings on aluminum silicate, in high aluminum soil, and on quartz surfaces. They speculated that the capacity of amorphous coatings would act as viscous bodies when moist and elastic bodies when dry and allows them to have a pronounced effect on the porous body as a whole. They further indicated that amorphous materials such as

those in gel-like substances lose their viscous properties irreversibly upon drying in high oxide systems but appear to be able to alter reversibly between the viscous and elastic state in high silicon systems. Blackmore (1973) has also reported that when 50% of $Fe(OH)_3$ by weight was added to Na-montmorillonite, only 25% of the original clay was released by high speed stirring in a phyrophosphate solution. Kemper and Koch (1966) investigated the aggregate stabilities of soils from Western United States and Canada and attempted to relate these stabilities to several factors including dehydration period and temperature. In general, however, very little work has been done on Typic Hydrandepts, or similar soils, to investigate whether restoration of original properties after drying is possible (El-Swaify and Lim, 1976).

MATERIALS AND METHODS

A. Materials

1. Soils: Selected soils for this study were:

   a. Akaka silty clay loam

   b. Hilo silty clay loam

   c. Kawaihae very fine sandy loam

Some background information on each soil are listed in Table 1.

As shown in the table, these three soils were developed originally from volcanic ash. The original ash is presumed to be the same, but due to different climate, particularly rainfall regimes, appreciable differences exist between the properties of the soils. These are mainly reflected in different profile characteristics, chemical and physical properties, and mineralogy, including amorphous and organic matter contents. These have been discussed earlier by Voss (1969), Chan (1972), Dias (1965), Gardiner (1967), Sato et al. (1973), and Foote et al. (1972).

2. Synthetic minerals

   a. Iron hydrous oxide (A).

   b. Iron hydrous oxide (B).

   c. Aluminum hydroxide (gibbsite/bayerite).

Table 1. Some Information on Selected Soils

Soils	Soil Classification: U. S. Taxonomy System	Soil Classification: Great Soil Group System	Origin	Elevation (m) of Occurrence	Rainfall (mm/year)	Total Area in Hawaii (ha)
Akaka	Thixotropic, isomesic, Typic Hydrandepts.	Hydrol Humic Latosol	Volcanic ash	300-1,400	about 7,600	46,400
Hilo	Thixotropic, isohyperthermic, Typic Hydrandepts.	Hydrol Humic Latosol	Volcanic ash	near sea level to 240	3,050-4,600	5,750
Kawaihae	Fine loamy, mixed isohyperthermic, Ustollic Camorthids.	Red Desert	Volcanic	near sea level to 450	130-500	11,730

B. Methods

1. Soil preparation

a. Soil sampling. All three soils are located on the island of Hawaii. Surface soils were collected at depths between 10 and 30 cm to avoid inclusion of the top portion of the soil which may be subject to some drying by exposure to the atmosphere.

b. Organic matter removal. Hydrogen peroxide treatment was applied to 50 g of each soil following the procedure of Kunze (1965). Approximately 100 ml of water was added to 50 g of each soil to make soil to water ratio 1:2. Ten to twenty ml of 30% hydrogen peroxide was added to the mixture, stirred, and the excess liquid was allowed to evaporate to keep soil to water ratio between 1:1 and 1:2 during digestion at 65°C - 70°C on a hot plate while covering with ribbed watchglass. This procedure was repeated until excessive effervescence ceased and the dark color was lost. Total hydrogen peroxide amounts added were 1,570 ml, 1,350 ml, and 950 ml for Akaka, Hilo, and Kawaihae soils, respectively.

2. Synthesis of hydroxides

The above three minerals were synthesized following the methods described by El-Swaify and Emerson (1975) for goethite, and by Gastuche (1964) for gibbsite.

a. Fe hydrous oxides. Iron hydrous oxides were synthesized from N $FeCl_3$ solutions by slow titration (more than 4 hours for 2 liters of $FeCl_3$ solution) with N NaOH up to pH levels of 6.0 and 12.0 for the Fe hydrous oxide (A) and Fe hydrous oxide (B), respectively.

b. Gibbsite. This aluminum hydroxide was synthesized from 0.1N-$AlCl_3$ solution by slow titration (more than 8 hours for 2 liters of $AlCl_3$ solution) with 0.1N-NaOH up to pH 4.5. All precipitated hydroxides were dialyzed against deionized water in bags of semi-permeable visking cellulose until free of Cl^-. This was ascertained by $AgNO_3$ testing. A period of 2-3 weeks was needed during which distilled water was changed twice a day.

3. Drying treatments

a. Oven drying. Ten to twenty g of soil or synthesized mineral was oven dried at 105°C for periods ranging from 24 to 48 hours until a constant weight

was obtained.

b. P_2O_5 drying. Ten to twenty g of soil or mineral were placed in a desiccator over P_2O_5 (anhydrous phosphorus pentoxide) for three weeks or until a constant weight was obtained.

c. Freeze drying. Twenty g of soil were suspended in distilled water by a mild blending treatment for a few minutes to provide a uniform dispersion. Suspended soils and synthesized minerals were frozen quickly in liquid nitrogen in Pyrex flasks then freeze-dried using a Virtis freeze dryer. Periods up to 5 days, depending on sample size, were required for complete drying.

4. Moisture content measurements

Soil samples, approximately 5 g each, were used to determine drying times. These were placed in a desiccator over P_2O_5 or in the oven at 105°C and weighed every 24 hours for 46 days. Moisture contents of soils and synthesized minerals which were subjected to drying treatments were measured by oven drying of subsamples taken immediately after the drying treatment.

5. Physical property measurements

a. Determination of shaking period for effective

aggregate breakdown. Ten g samples each of original and P_2O_5 dried soils were shaken for 5, 10, 20, 30, and 60 minutes (the last only for Akaka soil) in soil:water mixtures with a ratio 1:8, 1:6, and 1:4 for Akaka, Hilo, and Kawaihae soils, respectively. A Spex mixer mill (Model 1800) was used. The mixture was made to a volume of 250 ml. The concentration of released <2 μm particles in this suspension was measured using a plummet balance (modified from Marshall, 1956) at a depth of 5 cm after a settling time of 4 hours. Also, the concentration of sand-sized particles was determined from <53 μm readings determined by the plummet balance.

b. Determination of optimum soil:water ratio for particle breakdown. Two g (oven dry basis) of original and P_2O_5 dried soils were shaken as above for 20 minutes in mixtures with soil:water ratios of 1:2, 1:4, 1:6, 1:8, or 1:10. Contents of <2 μm particles were determined by the plummet balance and >53 μm particles directly by sieving through 270 mesh sieve after <2 μm measurement.

c. Analysis of particle size distribution. Five to twenty g samples were shaken in the Spex mixer mill

applying in mixtures containing 1:8, 1:6, or 1:4 soil:water for undried Akaka and mineral samples, undried Hilo, or Kawaihae and samples subjected to drying treatments, respectively. A shaking period of 20 minutes was used for all samples. After shaking, samples were suspended in 1 liter cylinders using distilled water and <2 μm particles were measured at a depth of 20 cm after a settling time of 16 hours.

To determine the chemical conditions favoring effective dispersion, a series of samples each weighing 10 or 20 g (oven dry basis) of original and P_2O_5-dried soils were shaken as above but in media adjusted to various pH values. This was achieved by adding adequate amounts of N HCl or N NaOh and distilled water. Final pH values ranged from 3 to 11. The soil:solution ratio was 1:4 and the shaking period 20 minutes. After suspending in 1 liter cylinders using distilled water, particles of <53 μ m and <2 μm effective diameter were measured after settling times of 80 seconds and 16 hours, respectively, at 20 cm depth.

d. Measurement of water retention. Sample tablets, each containing approximately 0.5 to 1.0 g samples,

were made from dried samples in a special mold using pressures of around 120 atmosphere (4,400 psi) by a Carver hydraulic press (Model B). Resulting discs were 0.5 cm in thickness and 1.3 cm in diameter. Water retention was measured at 10 and 50 cm suctions by these discs after an equilibrium period of 2 weeks. The measurements were made in specially designed units consisting of ceramic plates mounted in plexiglass and equipped with hanging water columns and adequate covers to protect against evaporation. Water contents of these discs were determined by oven drying at 105°C.

e. Specific surface area measurement by water vapor sorption. Five subsamples each weighing 0.5 - 1.0 g were placed in weighing bottles, mixed with enough distilled water to exceed saturation, placed in desiccators with controlled relative humidities, then allowed to equilibrate for 2-3 weeks after evacuation. Saturated solutions of KNO_3, NaCl, $Mg(NO_3)_2 \cdot 6H_2O$, $MgCl_2 \cdot 6H_2O$, and $LiCl \cdot H_2O$ were used to control the relative humidities in these desiccators at 92.0%, 76.0%, 53.4%, 33.2%, and 12.0%, respectively. Water contents after equilibrium were obtained by oven drying. Resulting sorption

isotherms were analyzed by the B.E.T. theory (Brunauer et al., 1938) to obtain specific surface areas.

6. Chemical property measurements

   a. Organic matter determinations. Oxidizable organic matter was determined by the Walkley-Black method (Jackson, 1967).

   b. Total chemical analysis. Total chemical analysis was performed by x-ray fluorescence using an ARL quantometer (Model 7200).

   c. Fe and Al determination. Fe and Al were extracted from samples ground to 100 mesh with a sodium dithionite-sodium citrate solution containing $NaHCO_3$ buffer (Aguilera and Jackson, 1953, and Mehra and Jackson, 1958). Acidified ammonium oxalate as originally proposed by Tamm (1922) and later modified by Schwertmann (1964) and McKeague and Day (1966) was also used. Fe extracted in both solutions was determined by a Perkin Elmer (Model 303) atomic absorption spectrophotometer and Al colormetrically by a spectronic 20 colorimeter after developing a color with aluminon as described by Black (1965).

d. Surface charge measurement. Surface charge and zero point of charge were measured principally following the potentiometric methods of Parks and de Bruyn, 1962; Atkinson et al., 1967; and El-Swaify and Sayegh, 1975. A series of samples weighing 0.5 to 1.0 g were each suspended in 100 ml of supporting electrolyte solutions at three concentrations. These were H_2O, 0.01N KCl, and 0.1N KCl. Appropriate amounts of N HCl or N KOH were added to obtain pH values in the range of 3.0 - 11.0 in each series and kept overnight. All pH measurements were made by a Beckman expandomatic (Model 76A) pH-meter.

7. Mineralogical identification

X-ray diffraction analysis was carried out by a Philips Norelco x-ray diffractometer using Cu Kα radiation and a graphite monochrometer. Different sample preparations were followed for different purposes.

a. Mineralogical identification of soils and synthesized minerals. Two samples consisting of clay- and silt-sized particles from each soil were saturated, one with N $MgCl_2$ and the other with N KCl. Excess salts were washed out by repeated shaking and

centrifugation with distilled water until a negative reaction was obtained for Cl^- in the supernatant solution with $AgNO_3$. Resulting wet pastes were subjected to x-ray analysis on glass slides. Synthesized minerals were directly subjected to x-ray analysis without any pretreatment.

b. Mineralogical alterations due to drying. One to two g subsamples were ground to pass a 100 mesh sieve. The resulting material was placed in a standard bulk powder holder for x-ray diffraction analysis.

c. Peak intensity changes upon Fe and Al extraction. Samples subjected to the above two extractants were washed with distilled water and powdered as above for unextracted samples. These materials were placed in a standard bulk powder holder for x-ray diffraction analysis.

RESULTS AND DISCUSSION

A. The Basis for Moisture Content Determinations

1. Changes in water content of soils during the drying process

Water losses from field-moist soils during a 46-day drying period in an oven at 105°C and in an evacuated desiccator over P_2O_5 at 25°C are shown in Figure 3. The relative humidity (P/Po x 100) of an atmosphere overlying P_2O_5 in an evacuated desiccator at 25°C (room temperature) is, by definition, zero (O'Brien, 1948). However, an oven at 105°C (at which P/Po = 906 mm Hg) in equilibrium with a surrounding environment similar to that of an average laboratory at 25°C (for which P/Po = 0.75 and consequently Po = 0.75 x 23.8 = 17.9 mm Hg) would be at P/Po = 0.0198 or 2.0% relative humidity. According to this calculation, it may be expected that water loss from any soil in the oven would be less than over P_2O_5. Figure 3 shows that none of the soils follow this calculation. Rather, more water loss was noted by oven drying than over P_2O_5. The magnitude of observed differences between the two methods was in the order Akaka>Hilo>Kawaihae. However, these differences at a given time were almost identical in both Hydrandepts when comparison was made on a percentage basis (approximately 7%). Water was lost faster under oven drying and in the order

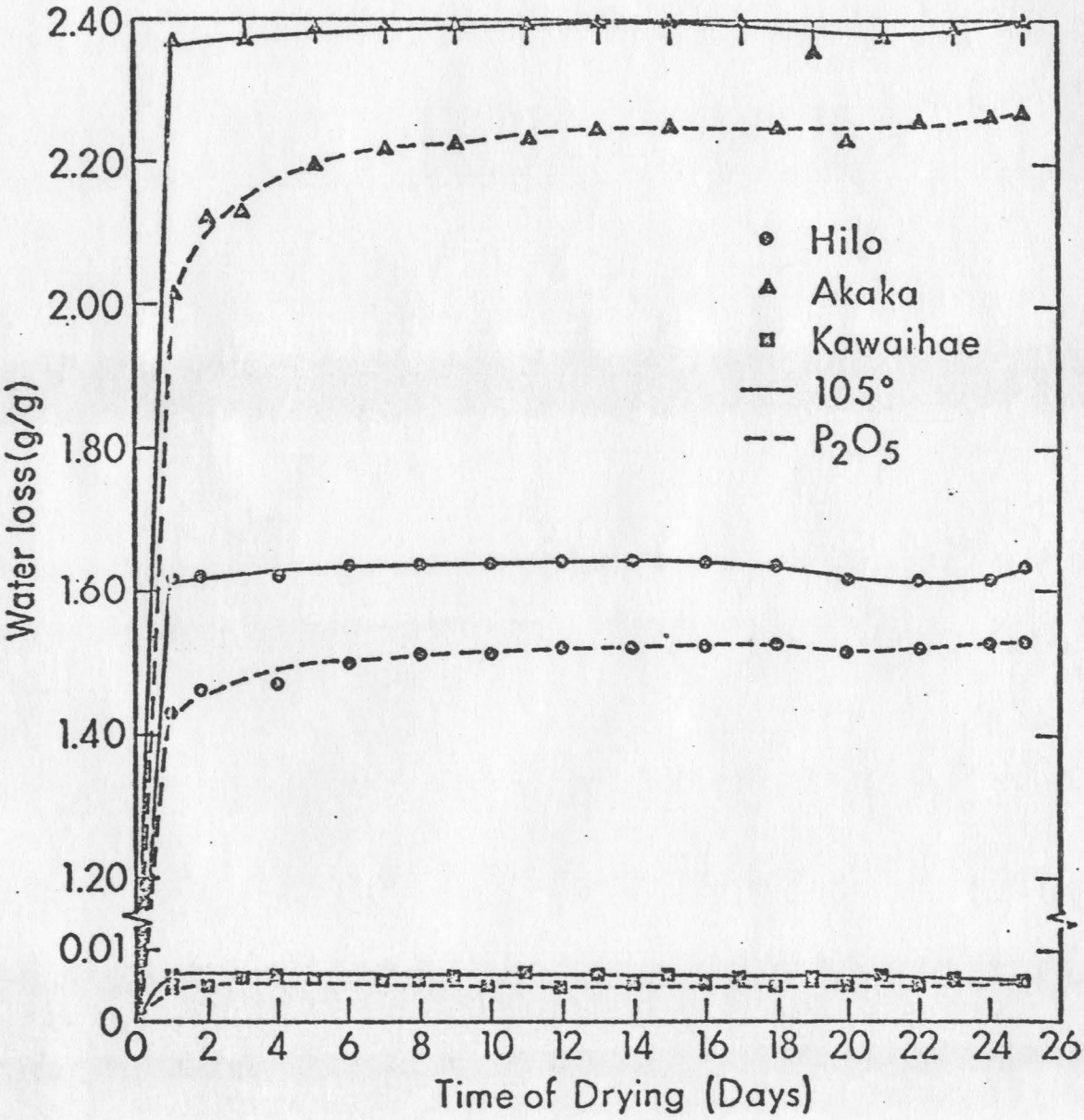

Figure 3. Loss of water from soils with time upon drying by various methods.

Kawaihae>Hilo>Akaka. The little effect of drying method on water loss from Kawaihae soil indicated that this soil may be treated as a reference soil.

2. Effect of drying method on water content at equilibrium

Table 2 shows the moisture contents of soil samples from each drying treatment as well as from field-moist condition which were placed in the oven at 105°C until equilibrium. The agreement between P_2O_5 and freeze drying is easily explained by the fact that the relative humidity in the evacuated freeze dry chamber is also zero. Freeze drying, however, is favored for conserving natural soil structure as there is less chance for soil particles to be pulled together by surface tension of an evaporating liquid medium as in oven or P_2O_5 drying cases. When conducted properly, frozen water is directly sublimated to vapor without giving a chance for liquid water to be present. When oven-dried and P_2O_5-dried samples were placed over P_2O_5 and in the oven, exchangeably, it was noted that oven-dried soils gained water by 3.56%, 3.23%, and 1.59% in Akaka, Hilo, and Kawaihae soils, respectively. However, these soils lost water by 8.71%, 5.63%, and 1.76% after a second cycle of oven drying. The reference, Kawaihae soil behaved normally in exhibiting complete reversibility of water loss or gain under the two conditions. It is, however, difficult to explain the higher water losses

Table 2. Water Contents of the Soils Subjected to Various Drying Methods at the End of Drying Period (Oven Dry Basis)

Method	Og%		
	Akaka	Hilo	Kawaihae
Original moisture	236.7	168.6	7.50
Air drying	26.3	21.1	7.30
Freeze drying	4.5	3.3	0.6
P_2O_5	4.8	3.2	0.9
Oven	0.00	0.00	0.00

as a result of the second than the first drying. The hysteresis phenomenon could be a reason whereby the efficiency of the first drying cycle was limited by incomplete diffusion of escaping H_2O molecules from the center to the outside of soil aggregates. In any case, when elevated temperature is involved during drying, structural water losses occur above and beyond the water present in a free or adsorbed state. Earlier, Weiser and Milligan (1934), elaborated on the dehydration process of synthetic gibbsite and presented an accurate dehydration isobar, plotting H_2O/Al_2O_3 mole ratio against temperature. This showed a very steep and complete decomposition in range 100°C - 200°C. In this temperature range, he showed that the H_2O/Al_2O_3 mole ratio changed from 3.0 to near 0.5 indicating a maximum possible water loss of 44.55% as a result of heating a pure gibbsite system. This supports the explanation that loss of structural water can occur by 105°C drying of gibbsite rich soils. Information presented by Jackson (1956) also indicate possible losses of structural water from gibbsite near 100°C. In addition, even though the formation of true "allophane" in Hydrandepts may not be favored due to their large contents of organic matter (Tokashiki and Wada, 1972), the presence of other amorphous constituents in both soils was confirmed. Such constituents probably possess a wide range of Si-O-Al structures to which silanol groups (OH) are attached with a vague boundary between

adsorbed and structural water. Such groups are more susceptible to loss when heat is involved in the drying process. Similarly, it is well known that goethite and lepidocrocite, both common monohydrated iron oxides which are present to variable extents in soils, including some Hydrandepts (El-Swaify and Lim, 1976) completely dehydrate at high temperature (above 250°C) to ferric oxides (Brown, 1972). Partial losses of structural water from such minerals may be encountered during oven-drying at 105°C.

B. Effects of Drying on Chemical and Mineralogical Properties

1. Estimation of total mineral contents

X-ray diffraction was the primary tool applied to identify the mineralogical composition of each soil. However, this alone was not sufficient because of various problems arising from structural similarities between minerals, deviation from strict three dimensional regularity and consequently undesirable co-effects, practical Hendricks-Teller dilution, differential x-ray absorption, a wide variety of crystal size and crystal orientation effects which hinder the estimation of mineral contents qualitatively and quantitatively. Therefore, total chemical analysis was also performed (Table 3).[1] The effects of drying were observed by comparing

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[1]Chemical analysis courtesy of Dr. R. C. Jones.

Table 3. Total Chemical Analysis (%)
by X-ray Fluorescence
(Oven Dried Basis)

	Akaka		Hilo		Kawaihae	
Components	Original	P_2O_5	Original	P_2O_5	Original	P_2O_5
SiO_2	10.10	10.51	8.03	7.98	23.46	23.95
Al_2O_3	21.36	22.85	29.49	32.30	27.16	27.57
Fe_2O_3	22.77	22.35	23.57	24.32	24.90	25.18
MgO	0.66	0.89	0.76	0.73	1.24	1.47
CaO	0.00	0.00	0.00	0.00	0.51	0.56
Na_2O	0.14	0.13	0.27	0.26	0.27	0.38
K_2O	0.36	0.38	0.22	0.20	0.37	0.37
TiO_2	4.41	4.41	4.69	4.70	5.52	5.75
P_2O_5	0.44	0.38	0.84	0.85	0.56	0.57
MnO	0.12	0.11	0.27	0.23	0.28	0.29
L.O.I.	40.87	38.03	33.05	28.01	15.69	14.57
Total	101.23	100.04	101.19	99.58	99.96	100.64

original and P_2O_5-dried soils. As shown in Table 3, all soils, particularly the two Hydrandepts, exhibit the silica deficit and sesquioxide enrichment which is typical of soil forming reactions in tropical regions. The higher enrichment of Typic Hydrandepts in sesquioxides is even more clear when corrections for LOI (loss on ignition) are made. An increased weight loss on ignition is also noted with increasing rainfall, which means that more hydrated minerals are present. Drying over P_2O_5 caused a decreased weight loss on ignition in each soil with the least loss noted in Kawaihae soil. When comparing Tables 3 and 4, it is observed that the amount of water loss is related to the amount of amorphous materials in the soils. As discussed in the above section, this also appears to coincide with higher water loss in a second cycle of oven drying.

Estimated major mineral contents of these three soils based on x-ray diffraction analysis and total chemical analysis are shown in Table 4. Mineralogical and certain physico-chemical properties were reported by Lai and Swindale (1967), Dias (1965), Voss (1969), Chan (1972), for Akaka and Hilo soils and by Gardiner (1967) for Kawaihae soil. Considering the relationship between rainfall and soil weathering, the sequential distribution of amorphous material in these three soils is rather obvious. Voss (1969) indicated a negative correlation between the contents of gibbsite and noncrystalline constituents in Hilo

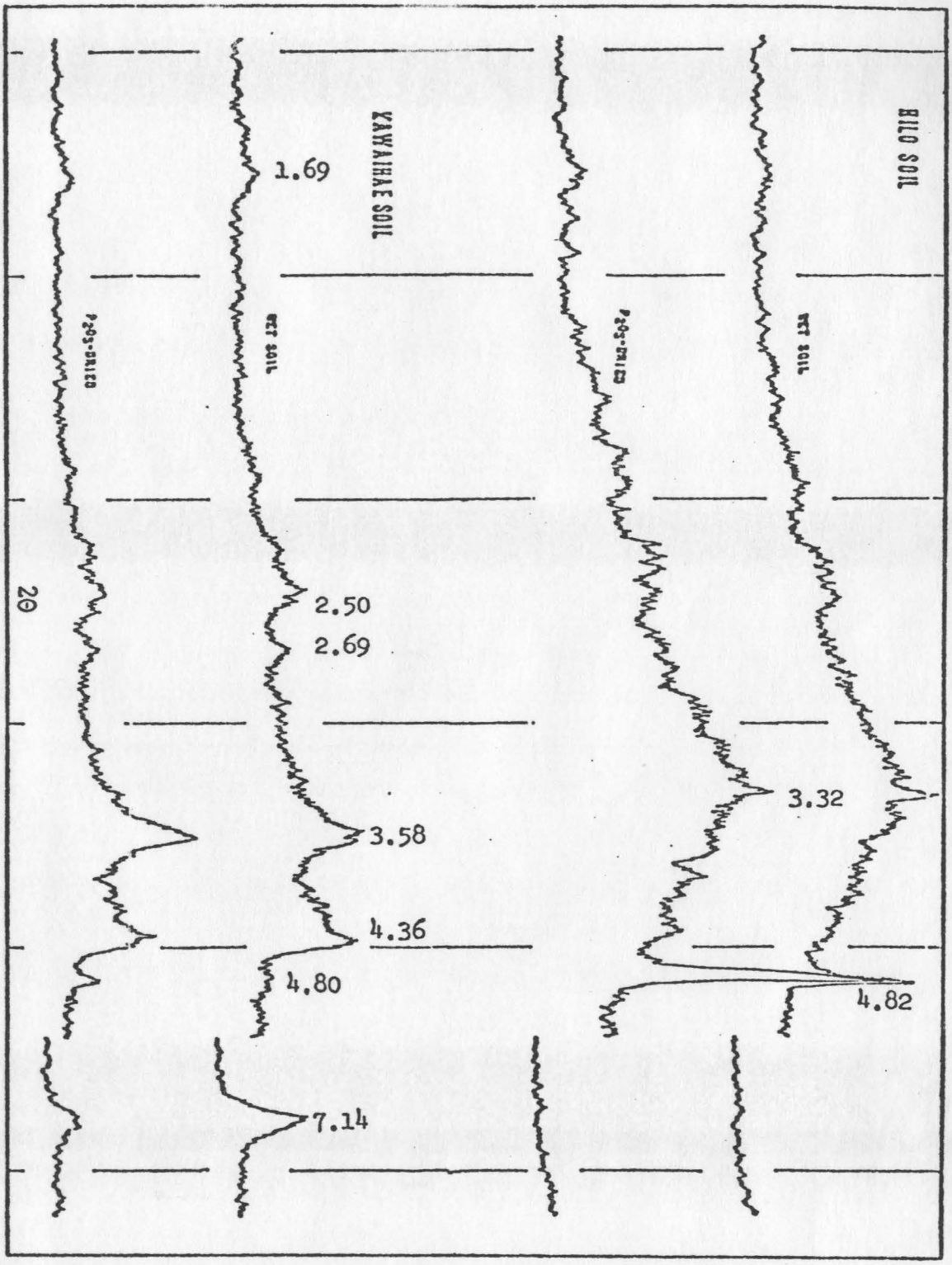
Table 4. Estimated Contents of Major Minerals (5 - 20 cm Depth)

Minerals	Akaka	Hilo	Kawaihae
dehydrated halloysite	-	-	45-50
quartz	8-12	7- 8	5-10
gibbsite	1- 5	20-25	-
goethite	1- 5	-	15-20
hematite	-	-	1- 5
magnetite	-	-	1- 5
maghemite	-	-	1- 5
TiO_2	4- 6	4- 5	-
amorphous materials	75-80	60-65	20-25

and Akaka soils. The large amount of kaolin minerals in Kawaihae soil indicates that this soil is at a rather young stage of development compared to the other two. Cline (1955) reported that kaolin decreased with increasing rainfall.

The drying pretreatments had little effect on the mineralogical constituents detected by x-ray diffraction analysis (Figure 4). Thus, only increases in peak intensities and a lowering of amorphous bands were noted in the two Hydrandepts as a result of drying. This phenomenon is easily explained by both the dilution of samples examined in moist condition and by changes in mass absorption coefficients due to water presence. The latter could be demonstrated using attenuation coefficients based on moisture contents of original and dried Akaka soils. By this calculation, the required soil sample thicknesses for the same intensity were 0.47 mm and 0.1 mm for the original and dried soils, respectively. Effects of drying on diffractograms were not significantly different for H_2O_2-treated and untreated soils, except that the amorphous bands were lower and peak intensities slightly decreased by hydrogen peroxide treatment. Oxidation of organic matter by hydrogen peroxide has been known to degrade soil minerals (Douglas and Fiessinger, 1971). It was thought that the low pH level of the slurry during oxidation was responsible for mineral degradation and higher pH levels were recommended. Chan (1972) reported the same amorphous material content in Hilo soil

Figure 4. X-ray diffraction patterns for original and pre-dried soils.


HILO SOIL
WET SOIL
PRE-DRIED
3.32
4.82
KAWAIHAE SOIL
WET SOIL
PRE-DRIED
1.69
2.50
2.69
3.58
4.36
4.80
7.14
60
50
40
30
20
10
2θ

as in the present study and observed what he reported as imogolite by electron microscope technique. El-Swaify and Lim (1976) reported the presence of fine crystalline goethite in the Hilo soil.

X-ray analysis of synthesized hydrous oxides of iron showed that the β-FeOOH (akaganeite) which was precipitated and aged at pH 6.0 exhibited only a large "amorphous" hump in the undried state. After oven drying at 105°C this band was lowered and akaganeite peaks appeared. But after firing at 550°C, all this material turned, as expected, to α-Fe_2O_3 (hematite). The α-FeOOH (goethite) which was precipitated and aged at pH 12.0 exhibited a large hump as well as apparent goethite peaks in the undried condition, pure goethite peaks only after drying at 105°C, and α-Fe_2O_3 (hematite) peaks after firing at 550°C.

The goal for making these two Fe hydrous oxides was to mimic for the Fe hydrous oxides in the soils of present study, primarily in terms of mineral particle size and next in terms of identity. However, it was not possible to synthesize exactly the same mineral constituents as those in the soils. Adding to the difficulties are the differences in minerals identified by different workers in these soils (e.g., Chan, 1972; El-Swaify and Lim, 1976) furthermore are very sensitive to the chemical and physical conditions which favor the formation of certain minerals

(e.g., Gastuche, 1963 and Mackay, 1961). Notwithstanding these difficulties, two quite distinguishable size minerals (a gel-like small-sized hydrous oxide and much larger sized crystalline mineral) were obtained successfully. This was the primary concern in this present study. Differences between these two species will be clearly shown in the later sections. These two minerals will be referred to as Fe-hydrous oxide (A) and Fe-hydrous oxide (B), respectively.

Therefore, as expected, noncrystalline (or fine crystalline) and crystalline types of hydrous iron oxides were obtained successfully by this controlled titration and aging method.

On the other hand, the precipitated and aged $Al(OH)_3$ was identified as a mixture of gibbsite (γ-$Al_2O_3 \cdot 3H_2O$) and bayerite (α-$Al_2O_3 \cdot 3H_2O$) of around 70:30 ratio. Some workers (e.g., de Boer, Fertuin, and Steggerda, 1954a, 1954b) reported the existence of two varieties for each of the gibbsite and bayerite minerals. However, further details are out of the scope in this study.

2. Organic matter contents of soils

Organic carbon as measured by the Walkley-Black method was converted to 12.5%, 7.4%, and 2.0% organic matter of original Akaka, Hilo, and Kawaihae soils, respectively. The contents were reduced to 2.0%, 0.9%, and 0.2% in the

respective H_2O_2-treated samples. For the H_2O_2 treatment a total of 1,570 ml, 1,350 ml, and 950 ml of 30% H_2O_2 were required for Akaka, Hilo, and Kawaihae soils, respectively.

3. Extractable aluminum and iron measurements

Tables 5 and 6 show the amounts of iron (as Fe and Fe_2O_3) and aluminum (as Al and Al_2O_3) extracted by the buffered dithionite-citrate solution, and by acidified ammonium oxalate in darkness. Among the numerous methods available, these two methods have recently received wide use for removal of free or "active" iron oxides to aid in soil dispersion, for enhancing x-ray diffraction peaks of soil clays, and as pretreatments for differential thermal analysis and electron microscopic examinations. Some workers (Lundblad, 1934; McKeague and Day, 1966) have also used the contents of such extractable sesquioxides as for classification of soils.

More iron was extracted with dithionite than with ammonium oxalate from Kawaihae soil. However, it is possible to detect significant differences between the Fe contents in extracts from Typic Hydrandepts only in the absence of drying treatments. In all cases, Fe extracted from both of these soils exceeded the Fe extracted from Kawaihae soil. In addition, no large differences appeared between the various drying treatments. Similarly, and although many of the H_2O_2-treated samples gave higher

Table 5. Percent Extractable Fe(Fe_2O_3) by Dithionite and Acidified Ammonium Oxalate Solutions

	Wet		Oven		P_2O_5		Freeze	
	Dithionite	Oxalate	Dithionite	Oxalate	Dithionite	Oxalate	Dithionite	Oxalate
				Akaka				
original	8.21(11.74)	6.53(9.34)	7.56(10.81)	7.64(10.94)	7.18(10.27)	8.21(11.74)	7.98(11.41)	7.18(10.27)
H_2O_2 treated	8.15(11.65)	8.16(11.67)	7.78(11.14)	8.46(12.10)	7.56(10.81)	8.64(12.36)	7.97(11.40)	8.60(12.30)
H_2O_2 control	7.64(10.92)	7.51(10.74)	6.74(9.61)	7.74(11.07)	8.62(12.33)	8.64(12.36)	7.58(10.84)	8.12(11.61)
				Hilo				
original	8.10(11.58)	6.32(9.04)	7.42(10.61)	5.84(8.35)	6.69(9.57)	6.48(9.78)	8.08(11.54)	6.96(9.95)
H_2O_2 treated	7.62(10.90)	7.83(11.20)	6.32(9.04)	6.19(8.85)	6.84(9.78)	7.44(10.64)	7.52(10.75)	8.06(11.53)
H_2O_2 control	7.29(10.42)	6.02(8.61)	7.81(11.17)	6.48(9.27)	6.85(9.80)	7.35(10.51)	8.64(12.36)	7.88(11.27)
				Kawaihae				
original	3.03(4.33)	1.20(1.72)	2.84(4.06)	1.05(1.50)	2.65(3.79)	1.18(1.69)	3.17(4.53)	1.11(1.59)
H_2O_2 treated	3.30(4.72)	1.32(1.89)	3.64(5.21)	0.92(1.32)	2.89(4.13)	1.14(1.63)	2.24(3.20)	1.03(1.47)
H_2O_2 control	3.83(5.48)	0.08(1.14)	2.71(3.88)	0.99(1.42)	2.61(3.73)	1.15(1.64)	3.50(5.01)	0.83(1.19)
				Synthetic Fe Hydrous Oxides				
Fe hydrous oxide (A)	41.21(58.93)	10.00(14.30)	23.84(34.09)	10.50(15.02)	22.24(3.20)	9.58(13.70)	33.51(47.92)	11.33(16.20)
Fe hydrous oxide (B)	16.65(23.81)	1.49(2.13)	12.15(17.37)	1.44(2.06)	18.27(26.13)	1.82(2.60)	16.65(23.81)	1.40(2.00)
commercial goethite (air dried)			3.72(5.32)	0.08(0.11)				

Table 6. Percent Extractable $Al(Al_2O_3)$ by Dithionite and Acidified Ammonium Oxalate Solutions

	Wet		Oven		P_2O_5		Freeze	
	Dithionite	Oxalate	Dithionite	Oxalate	Dithionite	Oxalate	Dithionite	Oxalate
				Akaka				
original	4.03 (7.62)	4.74(8.96)	3.74 (7.07)	5.28(9.98)	3.73 (7.05)	5.28(9.98)	3.58 (6.77)	4.96(9.37)
H_2O_2 treated	4.50 (8.51)	6.30(11.91)	4.50 (8.51)	5.28(9.98)	3.79 (7.16)	5.60(10.58)	4.50 (8.51)	5.26(9.94)
H_2O_2 control	4.35 (8.22)	5.59(10.57)	4.58 (8.65)	5.60(10.58)	6.41 (12.11)	5.00(9.45)	6.41 (12.11)	5.28(9.98)
				Hilo				
original	4.05 (7.65)	3.99(7.54)	3.36 (6.35)	3.80(7.18)	2.66 (5.03)	3.80(7.18)	3.49 (6.60)	3.80(7.18)
H_2O_2 treated	3.48 (6.43)	4.37(8.26)	2.62 (4.95)	3.43(6.48)	2.73 (5.16)	3.80(7.18)	3.26 (6.18)	4.64(8.77)
H_2O_2 control	3.70 (6.99)	3.78(7.14)	3.12 (5.90)	4.32(8.16)	2.70 (5.10)	3.80(7.18)	3.99 (7.54)	4.64(8.77)
				Kawaihae				
original	0.36 (0.68)	0.50(0.95)	0.37 (0.70)	0.56(1.06)	0.37 (0.70)	0.58(1.10)	0.31 (0.59)	0.60(1.13)
H_2O_2 treated	0.30 (0.57)	0.59(1.12)	0.30 (0.57)	0.58(1.10)	0.34 (0.64)	0.48(0.91)	0.32 (0.60)	0.50(0.95)
H_2O_2 control	0.37 (0.70)	0.63(1.19)	0.34 (0.64)	0.51(0.96)	0.36 (0.68)	0.48(0.91)	0.27 (0.51)	0.44(0.83)
				Synthetic Gibbsite/Bayerite				
original	0.068(0.13)	4.60(8.69)	0.068(0.13)	3.42(6.46)	0.068(0.13)	4.24(8.01)	0.068(0.13)	3.93(7.43)

extractable Fe (probably due to released chelated Fe from oxidized organic matter), only minor differences were noted between hydrogen peroxide treated and untreated samples. For synthetic minerals, dithionite extracted more Fe than did ammonium oxalate emphasizing the more selective nature of the latter. Much more Fe was extracted from Fe hydrous oxide (A) than from Fe hydrous oxide (B), as expected. However, the ratio Fe (dithionite):Fe (oxalate) was much larger in Fe hydrous oxide (B). Differences between Fe extracted from samples subject to various drying treatments were more pronounced in Fe hydrous oxide (A), particularly in dithionite. This confirmed the selective nature of the oxalate solution whereas the dithionite appeared to dissolve Fe in direct proportion to the extent of exposed surface.

For extracted aluminum, Table 6 shows that oxalate extracts always had higher Al than dithionite in all soils and in synthesized Al hydroxide. The difference between two extracts was most notable in the Al hydroxide. The total amount extracted was similar in the two Typic Hydrandepts but was higher for both than for the Kawaihae soils. As with Fe, no differences were observed between drying treatments or due to hydrogen peroxide treatment.

McKeague and Day (1966) reported that both extractable Fe and Al values were useful in studies of soil genesis

and classification. The oxalate values gave an approximation of degree of accumulation of amorphous products of recent weathering and the dithionite Fe values approximated the combined contents of amorphous Fe and of crystalline Fe oxides. Results in Table 5 agree with those of McKeague and Day (1966) when considering the contents of amorphous constituents in these soils (Table 4), and when comparing the two synthesized iron hydrous oxides. Interestingly, the iron extracted from Fe hydrous oxide (B) were about the same as those of McKeague and Day (1966) with as slight difference for the oxalate extract. Results of Blume and Schwertmann (1969), Pawluk (1972), and Schwertmann (1973) also agreed with the data presented here. Accordingly, it may be concluded that the absence of strong differences between the contents of extracts from samples subjected to various drying treatments and H_2O_2 treated and untreated soils, that none of those treatments resulted in significant alteration of crystallinity. Similar observations and conclusions may be made for extractable Al in both extractants (Table 6), except that the oxalate appeared to be a stronger and more effective extractant for amorphous forms Al than dithionite (McKeague and Day, 1966).

4. Changes in x-ray diffraction patterns due to Al and Fe extraction

Many extractants and methods have been suggested to remove

free Fe and Al for improvement of x-ray diffraction peaks that are otherwise difficult or impossible to detect. Among these, solutions of sodium dithionite (Jackson, 1956), ammonium oxalate (Schwertmann, 1964), and calcium chloride (Tweneboah, 1967) have been given recent emphasis. Figures 5 and 6 show the effects of oxalate and dithionite extractant treatments on x-ray diffraction patterns of soils and synthesized minerals. These soils show that both extractions generally enhanced peak intensities equally, with occasionally more enhancement with dithionite extraction. This occurred regardless of hydrogen peroxide pretreatment. However, the two synthetic hydrous oxides of iron exhibited no significant changes due to either extraction. On the other hand, peak intensities for the aluminum hydroxide system were much more enhanced by oxalate extraction than by dithionite extraction.

Pawluk (1972) reported increased x-ray diffraction peak intensities of soils but decreased intensities when extraction was further continued with either extractant. The early enhancement due to both extractions are easily explained by the removal of particle coatings which are generally thick and presumed to be amorphous material in nature (Jones and Uehara, 1973). Once such coatings are removed, further extractions may result in attacking the particles themselves, thus causing their degradation. This second stage may not be easily reached for soils with very

Figure 5. X-ray diffraction patterns for soils before and after extraction with oxalate and dithionite extraction.

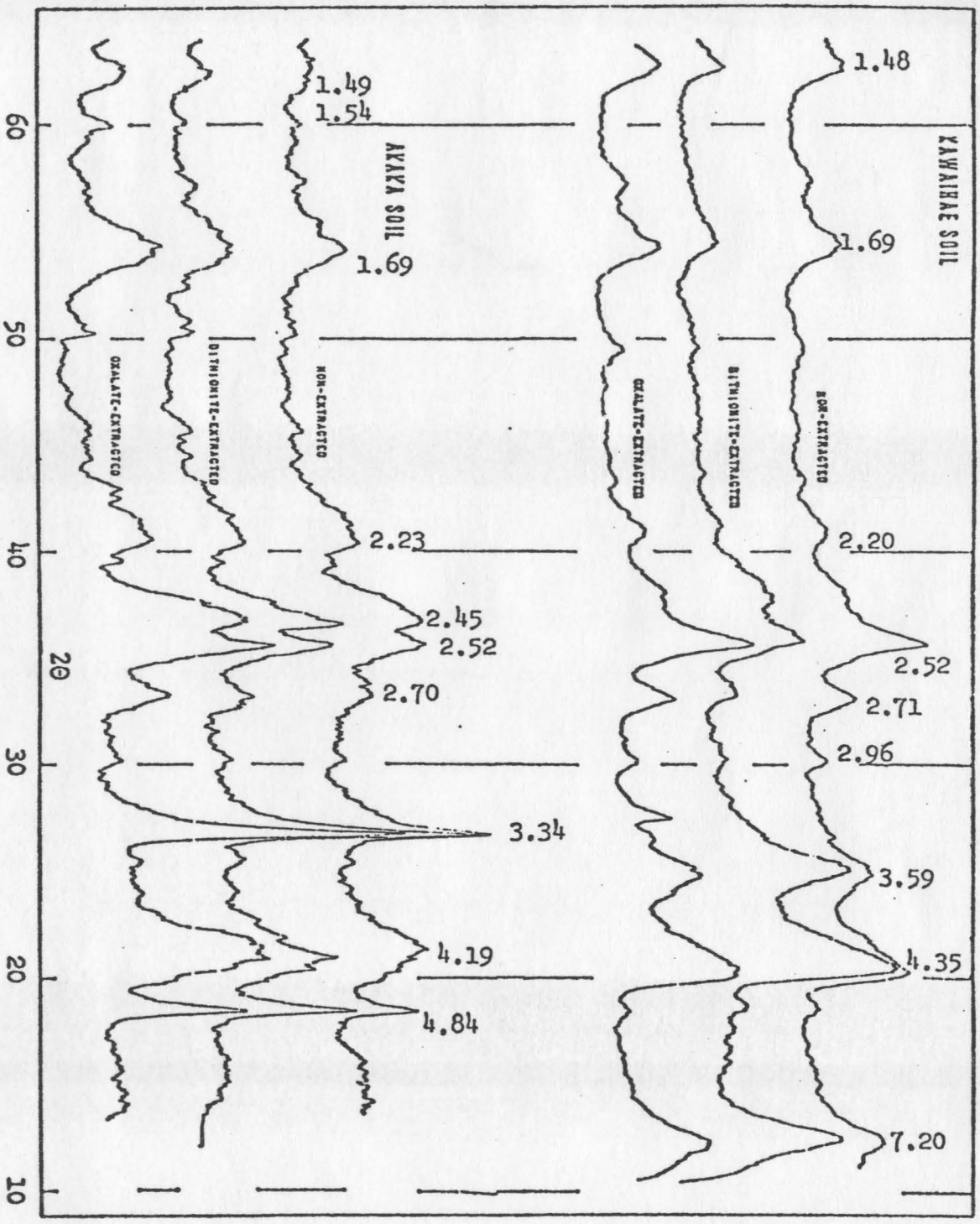
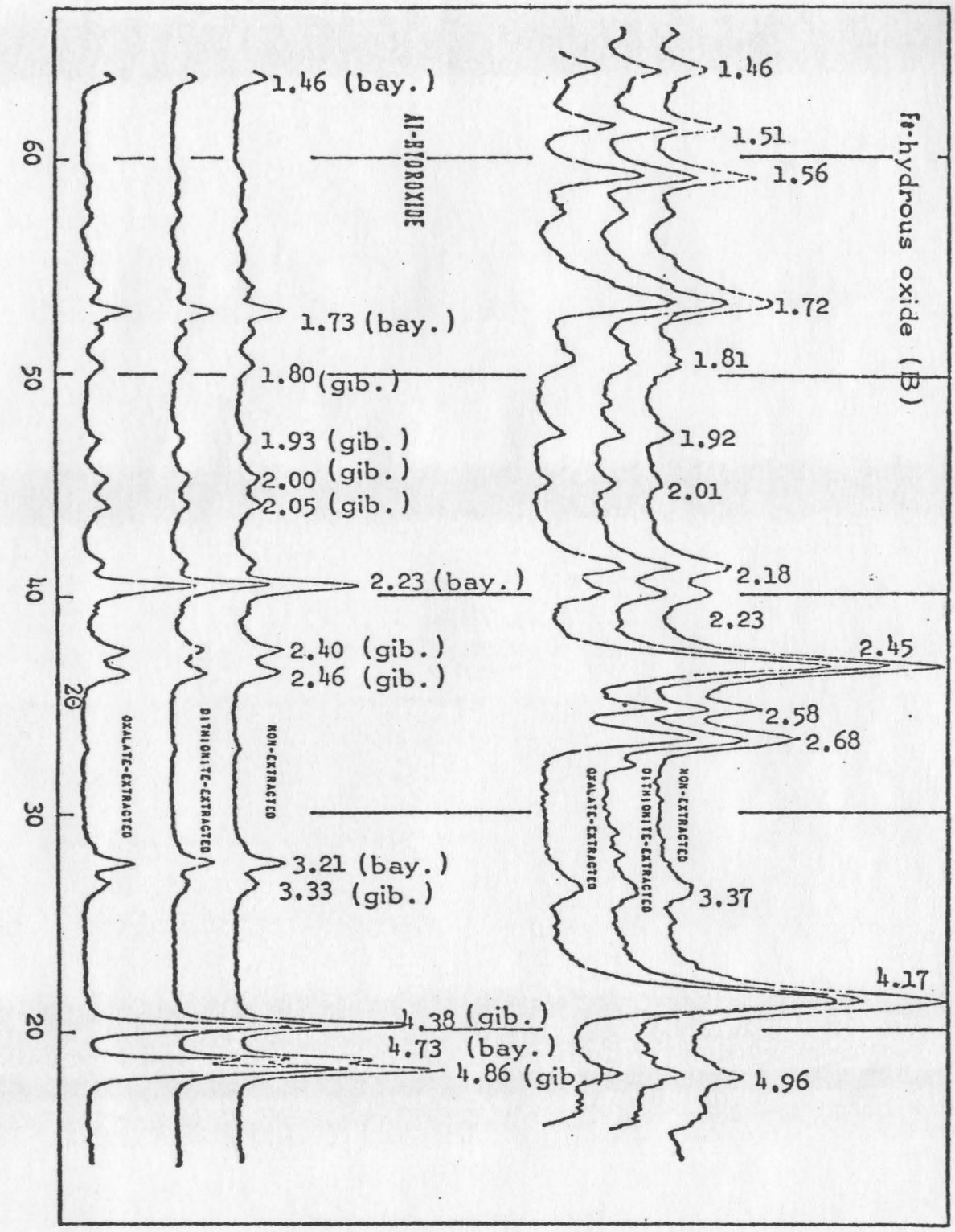

AKAKA SOIL
KAWAIHAE SOIL
OXALATE-EXTRACTED
DITHIONITE-EXTRACTED
NON-EXTRACTED
1.49
1.54
1.69
2.23
2.45
2.52
2.70
3.34
4.19
4.84
1.48
1.69
2.20
2.52
2.71
2.96
3.59
4.35
7.20
60
50
40
30
20
10
2θ

Figure 6. X-ray diffraction patterns for Fe and Al hydroxides before and after extraction with oxalate and dithionite extractants.


Al-hydroxide
Fe-hydrous oxide (B)
1.46 (bay.)
1.73 (bay.)
1.80 (gib.)
1.93 (gib.)
2.00 (gib.)
2.05 (gib.)
2.23 (bay.)
2.40 (gib.)
2.46 (gib.)
3.21 (bay.)
3.33 (gib.)
4.38 (gib.)
4.73 (bay.)
4.86 (gib.)
1.46
1.51
1.56
1.72
1.81
1.92
2.01
2.18
2.23
2.45
2.58
2.68
3.37
4.17
4.96
OXALATE-EXTRACTED
DITHIONITE-EXTRACTED
NON-EXTRACTED
60
50
40
30
20
2θ

large contents of amorphous materials. Judging from Fe extractability in dithionite of oven dried Fe hydrous oxide (A) (23.8%), chances are slim that all amorphous $Fe(OH)_3$ was removed from this system completely. Schwertmann speculated that such may be the case for the highly weathered soils in tropics with appreciable amounts of amorphous iron oxides. He gave the example of Segalen et al. (1971) who used a much stronger extractant (8N-HCl) to measure this fraction.

5. Charge characteristics

Surface charge characteristics of the soils and synthesized minerals were measured in H_2O and at two different concentrations of indifferent electrolyte (KCl) solutions by the potentiometric method (El-Swaify and Sayegh, 1975). Figures 7 through 12 show net adsorption densities of H^+ and OH^- (meq/g) as a function of pH as obtained for nontreated (original or non-dried) soils and synthesized minerals. These curves are considered as a measure of net charges associated with soils or minerals with the intersection point as the zero point of charge (Z.P.C.). Using exactly the same procedure, the effects of hydrogen peroxide, and of various drying treatments were compared, respectively (Table 7).

Table 8 shows Z.P.C. values for each system. Considering the mineralogical composition of these soils (Table 4), these

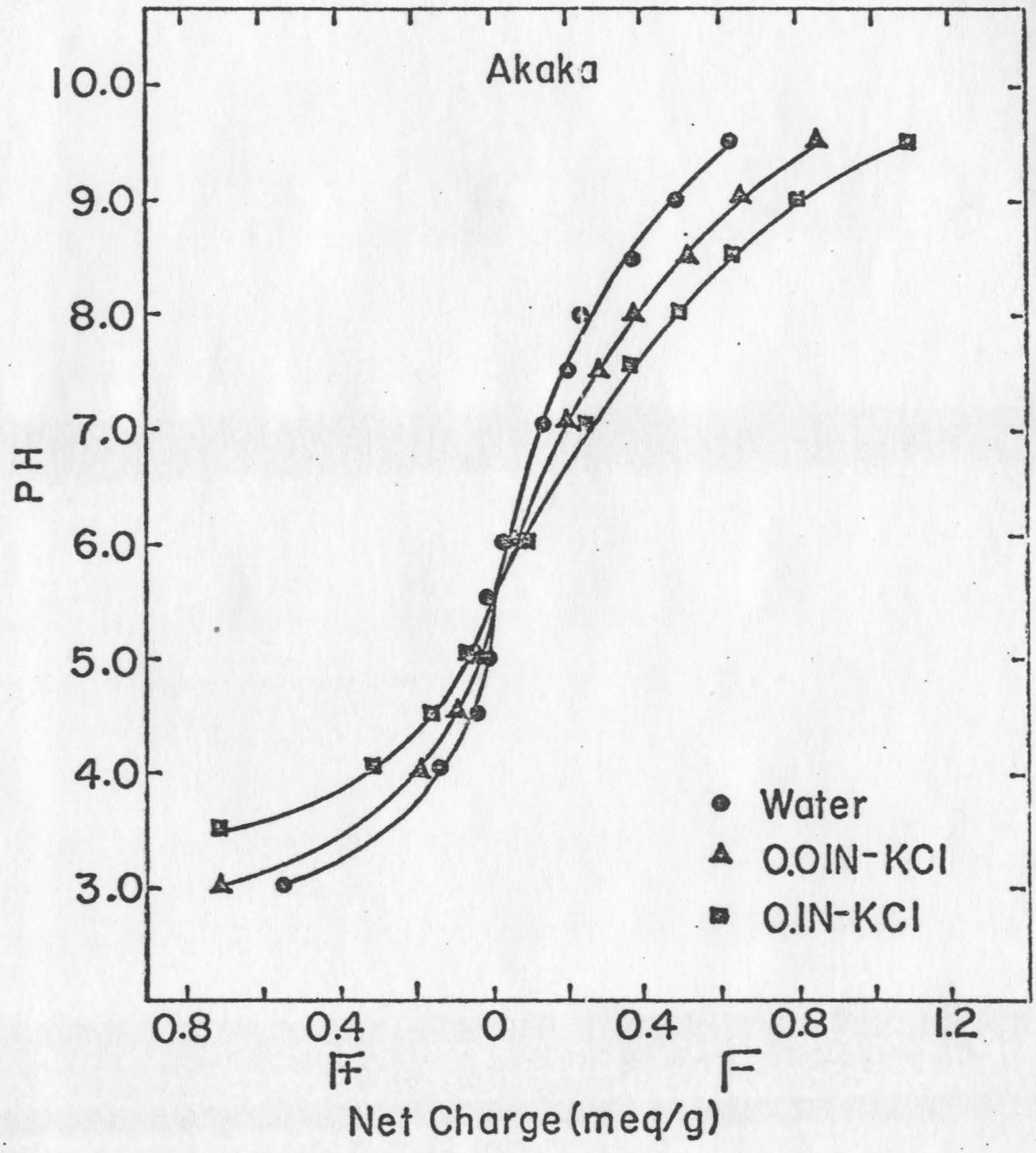


Figure 7. Net charge curves for Akaka soil.

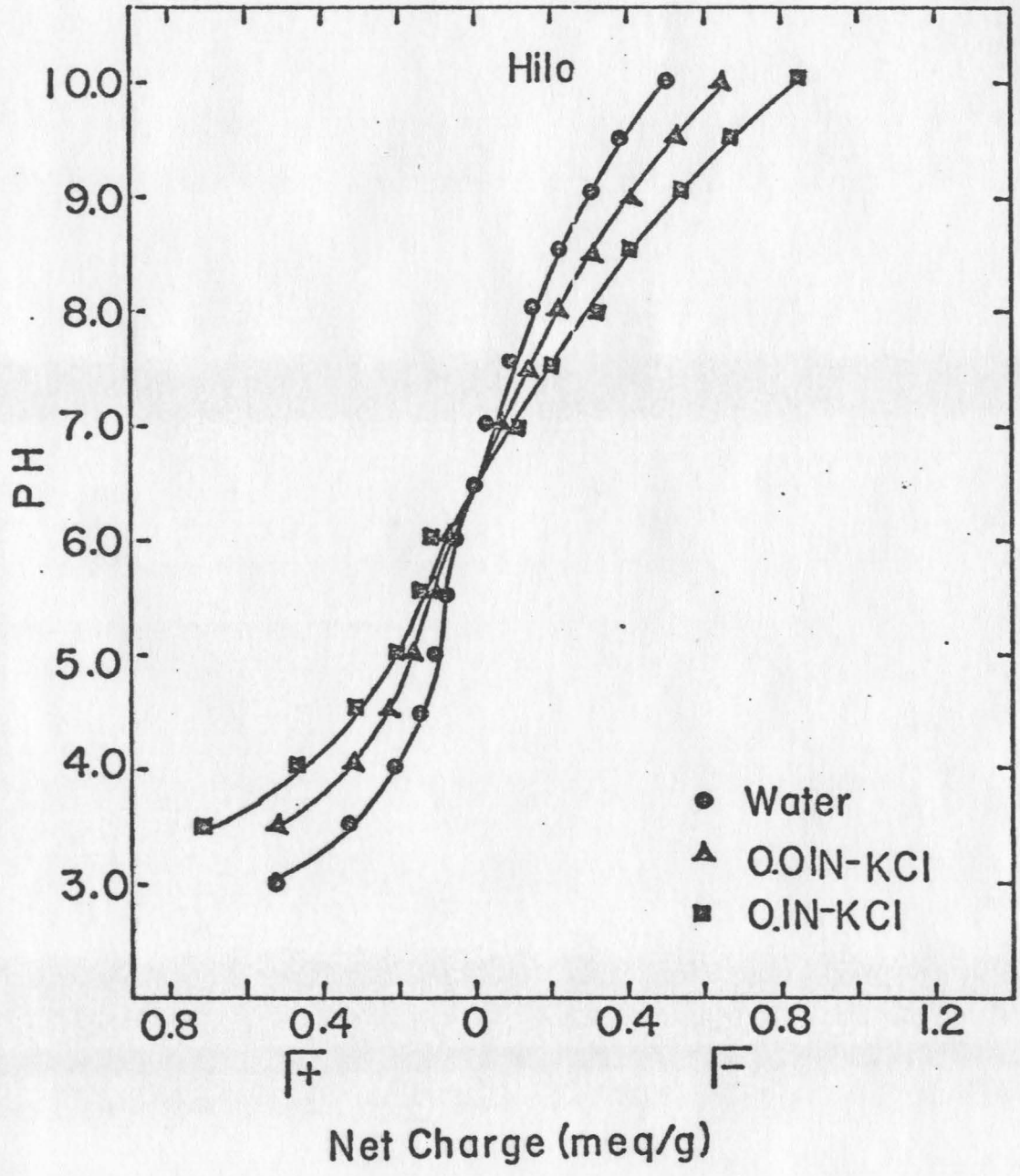


Figure 8. Net charge curves for Hilo soil.

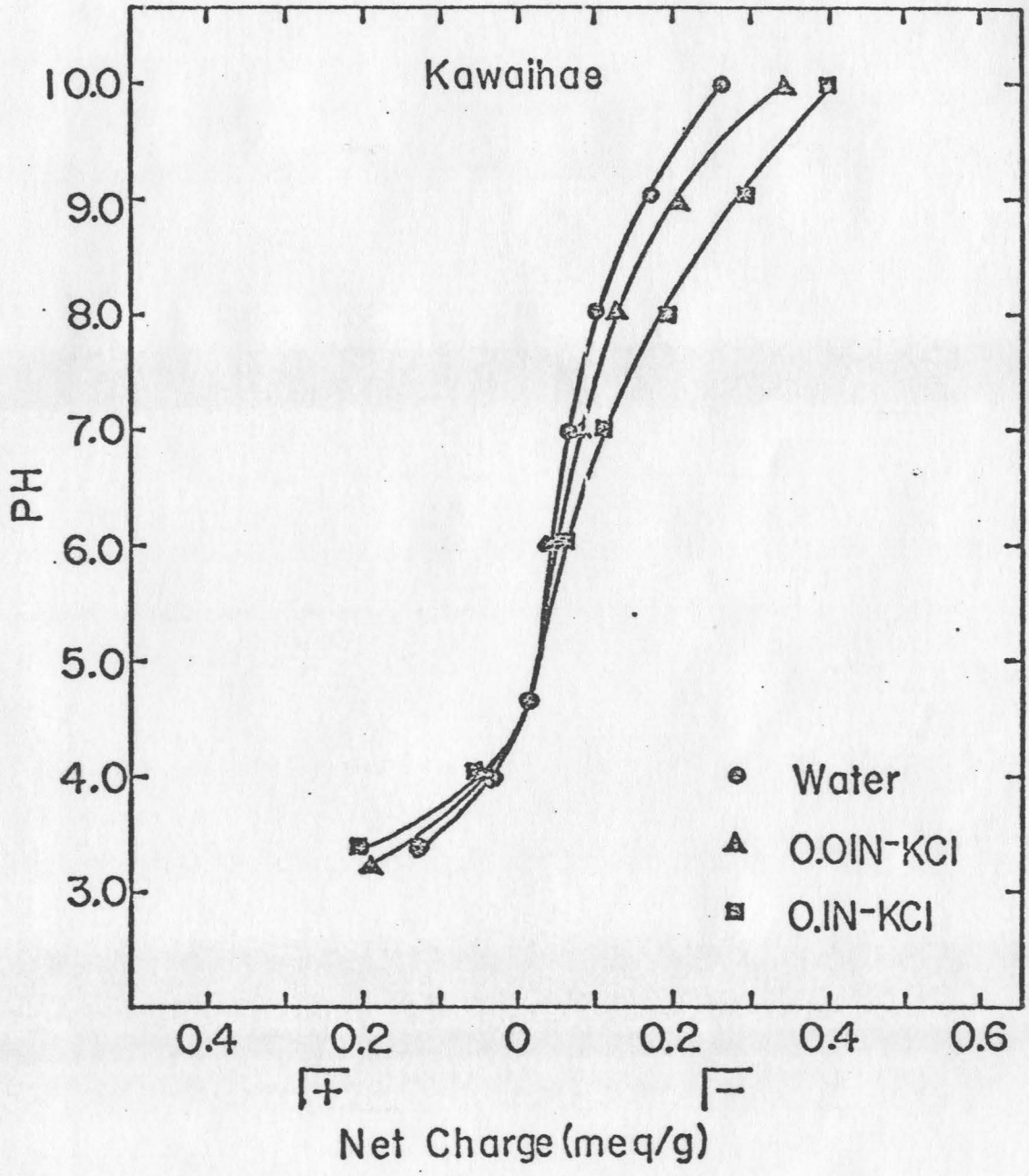


Figure 9. Net charge curves for Kawaihae soil.

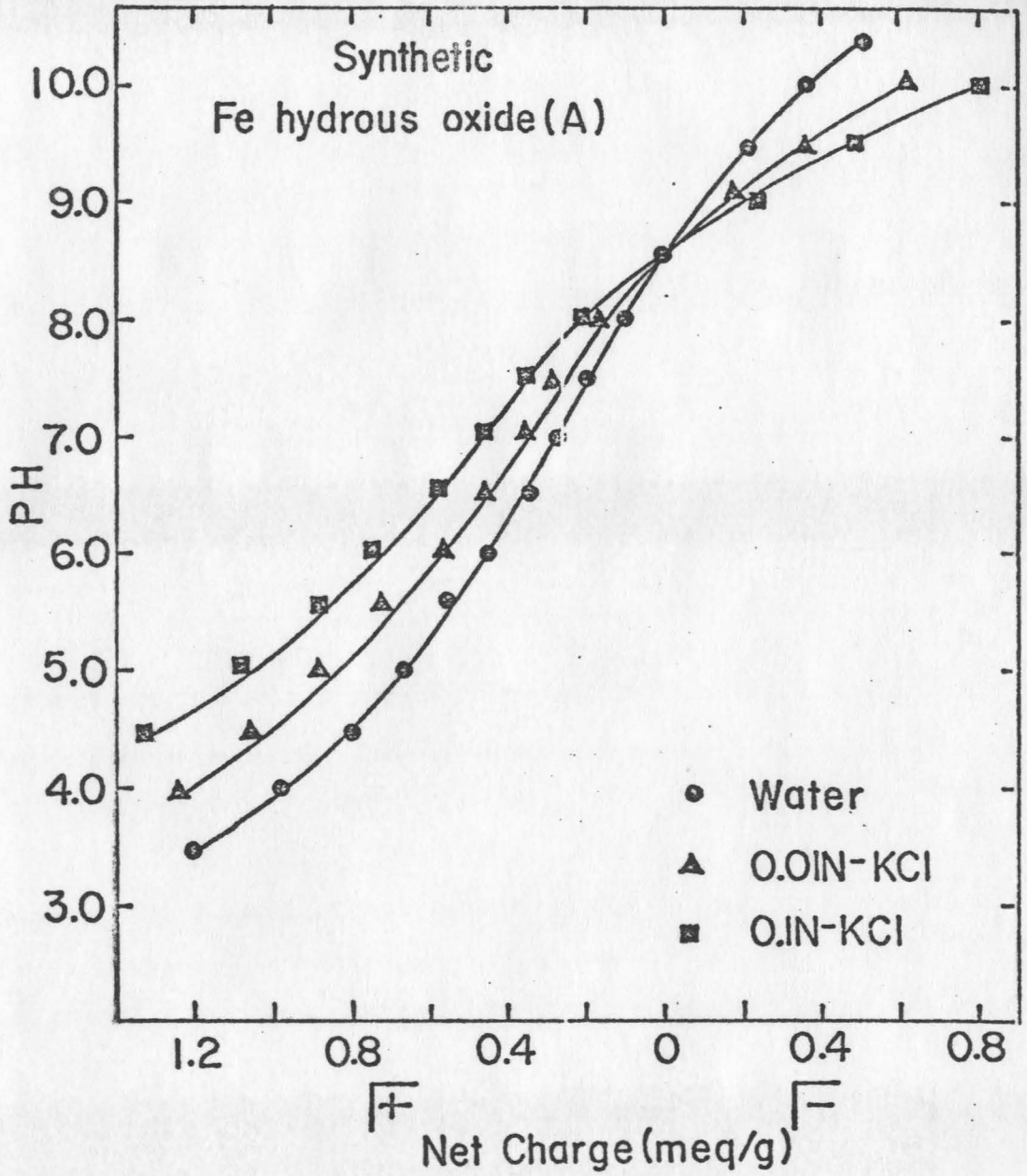


Figure 10. Net charge curves for Fe hydrous oxide (A).

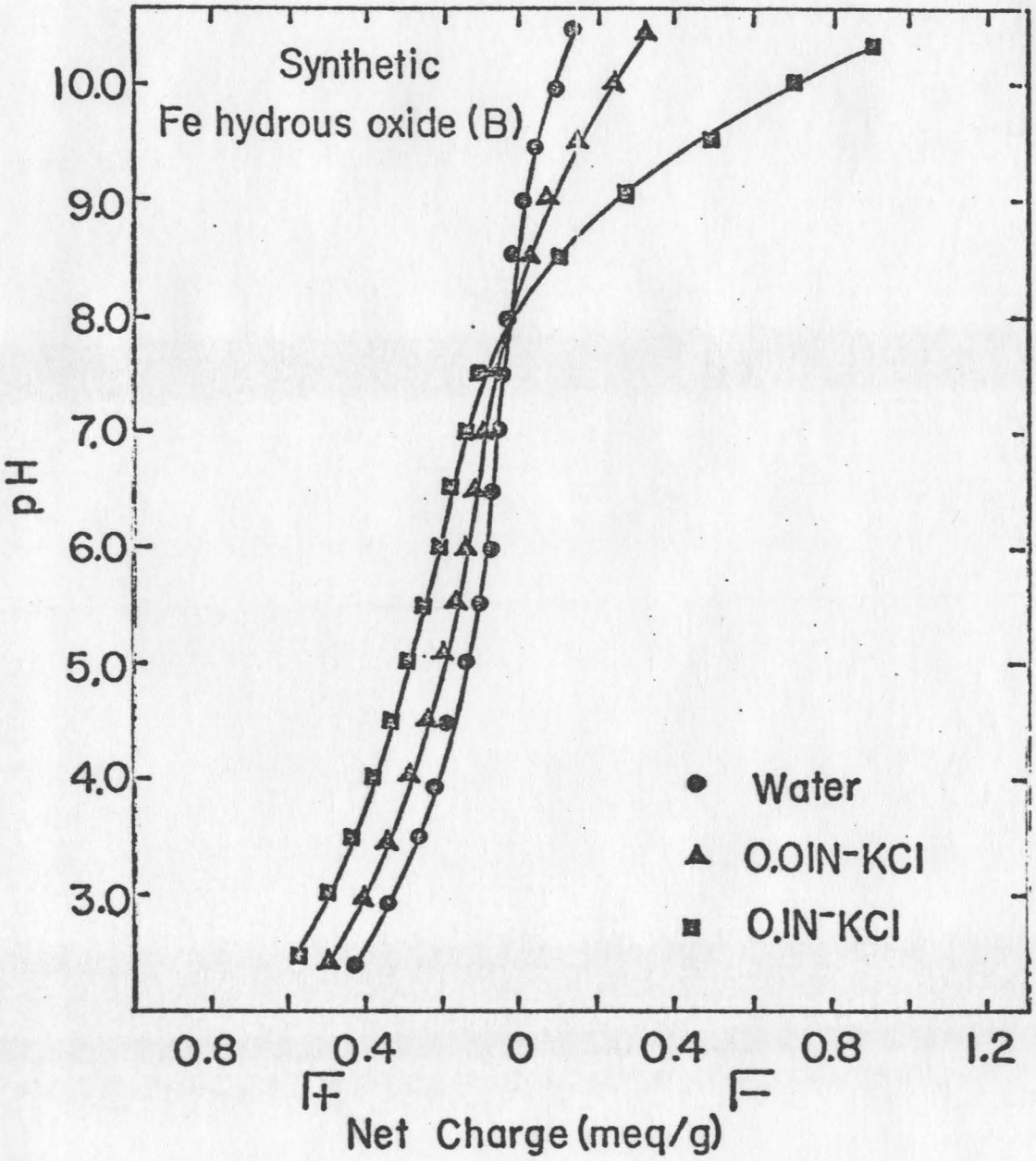


Figure 11. Net charge curves for Fe hydrous oxide (B).

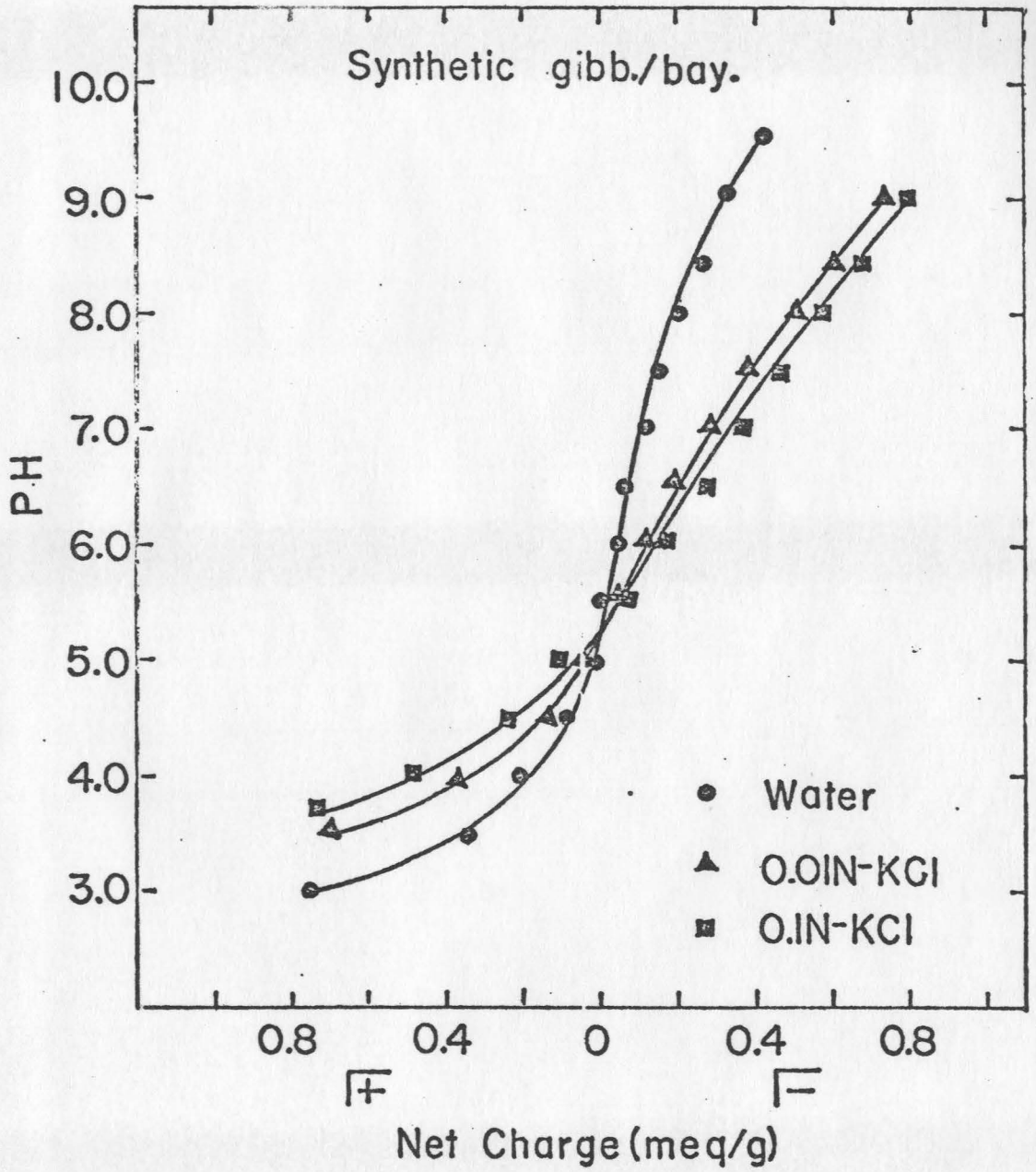


Figure 12. Net charge curves for synthetic Al-hydroxide.

Table 7. Dependence of Net Charge (meq/g) in Different Electrolyte Concentrations at Selected pH Values (Potentiometric Method)

pH	Wet			Oven			P_2O_5			Freeze		
	H_2O	0.01N KCl	0.1N KCl	H_2O	0.01N KCl	0.1N KCl	H_2O	0.01N KCl	0.1N KCl	H_2O	0.01N KCl	0.1N KCl
					Akaka							
					Original (untreated)							
3.5	+0.27	+0.36	+0.70	+0.05	+0.14	+0.38	+0.06	+0.18	+0.37	+0.18	+0.49	+0.76
5.0	+0.01	+0.03	+0.05	+0.01	+0.02	+0.05	+0.01	+0.04	+0.06	+0.02	+0.04	+0.08
7.0	-0.14	-0.20	-0.26	-0.04	-0.05	-0.06	-0.01	-0.05	-0.08	-0.11	-0.17	-0.26
8.0	-0.25	-0.37	-0.51	-0.06	-0.08	-0.10	-0.02	-0.08	-0.11	-0.27	-0.43	-0.51
9.5	-0.63	-0.85	-1.11	-0.08	-0.16	-0.40	-0.05	-0.22	-0.50	-0.55	-0.80	-1.04
					H_2O_2 treated							
3.5	+0.70	+0.86	+1.33	+0.14	+0.70	+1.10	+0.20	+0.61	+1.00	+0.88	+0.92	+1.03
5.0	+0.04	+0.08	+0.08	+0.05	+0.06	+0.10	+0.04	+0.08	+0.13	+0.02	+0.06	+0.08
7.0	-0.14	-0.16	-0.22	-0.03	-0.08	-0.10	-0.05	-0.07	-0.21	-0.25	-0.28	-0.34
8.0	-0.32	-0.44	-0.52	-0.13	-0.47	-0.41	-0.15	-0.36	-0.54	-0.45	-0.62	-0.68
9.5	-1.02	-1.12	-1.44	-0.39	-1.02	-1.11	-0.43	-1.06	-1.16	-0.94	-1.25	-1.43
					H_2O_2 control							
3.5	+0.35	+0.67	+0.85	+0.32	+0.55	+0.75	+0.22	+0.34	+0.98	+0.30	+0.66	+0.94
5.0	+0.01	+0.01	+0.02	+0.10	+0.12	+0.17	+0.01	+0.02	+0.03	+0.01	+0.015	+0.02
7.0	-0.13	-0.27	-0.38	-0.001	-0.02	-0.05	-0.03	-0.11	-0.22	-0.16	-0.27	-0.38
8.0	-0.29	-0.48	-0.66	-0.02	-0.15	-0.38	-0.04	-0.18	-0.40	-0.29	-0.48	-0.66
9.5	-0.74	-1.04	-1.25	-0.15	-0.58	-1.12	-0.11	-0.42	-1.04	-0.74	-1.04	-1.24

Table 7 (Continued). Dependence of Net Charge (meq/g) in Different Electrolyte Concentrations at Selected pH Values (Potentiometric Method)

pH	Wet			Oven			P_2O_5			Freeze		
	H_2O	0.01N KCl	0.1N KCl	H_2O	0.01N KCl	0.1N KCl	H_2O	0.01N KCl	0.1N KCl	H_2O	0.01N KCl	0.1N KCl
					Hilo							
					Original (untreated)							
3.5	+0.33	+0.52	+0.71	+0.15	+0.32	+0.50	+0.10	+0.25	+0.45	+0.43	+0.38	+0.72
5.0	+0.11	+0.18	+0.21	+0.01	+0.04	+0.11	+0.01	+0.03	+0.08	+0.08	+0.10	+0.22
7.0	-0.05	-0.08	-0.11	-0.01	-0.02	-0.04	-0.01	-0.02	-0.06	-0.07	-0.12	-0.15
8.0	-0.15	-0.22	-0.31	-0.05	-0.07	-0.12	-0.02	-0.09	-0.18	-0.16	-0.30	-0.33
9.5	-0.39	-0.52	-0.69	-0.10	-0.15	-0.51	-0.04	-0.20	-0.54	-0.43	-0.58	-0.66
					H_2O_2 treated							
3.5	+0.14	+0.65	+0.68	+0.18	+0.48	+0.55	+0.18	+0.49	+0.66	+0.26	+0.77	+0.84
5.0	+0.08	+0.19	+0.10	+0.03	+0.06	+0.11	+0.02	+0.05	+0.08	+0.03	+0.06	+0.08
7.0	-0.08	-0.11	-0.20	-0.05	-0.13	-0.18	-0.03	+0.07	+0.16	-0.05	-0.10	-0.15
8.0	-0.20	-0.27	-0.35	-0.15	-0.33	-0.44	-0.14	-0.29	-0.45	-0.32	-0.40	-0.50
9.5	-0.55	-0.64	-1.17	-0.31	-0.78	-0.94	-0.31	-0.72	-0.83	-0.73	-0.84	-0.97
					H_2O_2 control							
3.5	+0.36	+0.61	+0.75	+0.23	+0.56	+0.64	+0.14	+0.29	+0.58	+0.26	+0.71	+0.79
5.0	+0.07	+0.19	+0.14	+0.04	+0.06	+0.11	+0.01	+0.02	+0.05	+0.03	+0.05	+0.08
7.0	-0.08	-0.14	-0.14	-0.02	-0.12	-0.14	-0.02	-0.10	-0.17	-0.09	-0.21	-0.25
8.0	-0.25	-0.23	-0.38	-0.08	-0.24	-0.34	-0.06	-0.18	-0.30	-0.24	-0.33	-0.36
9.5	-0.59	-0.65	-1.26	-0.16	-0.42	-0.60	-0.22	-0.36	-0.69	-0.52	-0.79	-0.91

Table 7 (Continued). Dependence of Net Charge (meq/g) in Different Electrolyte Concentrations at Selected pH Values (Potentiometric Method)

pH	Wet			Oven			P_2O_5			Freeze		
	H_2O	0.01N KCl	0.1N KCl	H_2O	0.01N KCl	0.1N KCl	H_2O	0.01N KCl	0.1N KCl	H_2O	0.01N KCl	0.1N KCl
					Kawaihae							
					Original (untreated)							
3.5	+0.14	+0.16	+0.17	+0.03	+0.04	+0.06	+0.04	+0.05	+0.06	+0.06	+0.07	+0.09
5.0	-0.02	-0.02	-0.02	-0.02	-0.02	-0.02	-0.02	-0.02	-0.03	-0.02	-0.02	-0.03
7.0	-0.06	-0.08	-0.11	-0.04	-0.05	-0.08	-0.03	-0.06	-0.09	-0.04	-0.09	-0.10
8.0	-0.10	-0.12	-0.19	-0.07	-0.08	-0.13	-0.06	-0.09	-0.14	-0.11	-0.13	-0.17
9.5	-0.21	-0.26	-0.34	-0.17	-0.15	-0.25	-0.20	-0.21	-0.26	-0.20	-0.27	-0.34
					H_2O_2 treated							
3.5	+0.24	+0.26	+0.35	+0.12	+0.17	+0.23	+0.18	+0.24	+0.34	+0.13	+0.24	+0.27
5.0	-0.03	-0.04	-0.05	-0.01	-0.03	-0.04	-0.01	-0.02	-0.03	-0.01	-0.01	-0.02
7.0	-0.05	-0.07	-0.12	-0.04	-0.05	-0.08	-0.02	-0.04	-0.08	-0.02	-0.04	-0.08
8.0	-0.08	-0.09	-0.13	-0.06	-0.07	-0.10	-0.06	-0.08	-0.11	-0.04	-0.06	-0.12
9.5	-0.15	-0.25	-0.30	-0.12	-0.23	-0.28	-0.24	-0.28	-0.28	-0.15	-0.21	-0.25
					H_2O_2 control							
3.5	+0.20	+0.23	+0.38	+0.15	+0.18	+0.27	+0.20	+0.26	+0.32	+0.21	+0.22	-0.26
5.0	-0.03	-0.05	-0.06	-0.04	-0.05	-0.06	-0.04	-0.05	-0.06	-0.04	-0.06	-0.07
7.0	-0.04	-0.06	-0.12	-0.05	-0.06	-0.08	-0.06	-0.07	-0.08	-0.05	-0.08	-0.10
8.0	-0.07	-0.08	-0.14	-0.08	-0.08	-0.09	-0.08	-0.09	-0.10	-0.10	-0.17	-0.16
9.5	-0.18	-0.24	-0.28	-0.11	-0.21	-0.27	-0.10	-0.18	-0.22	-0.14	-0.23	-0.30

Table 7 (Continued). Dependence of Net Charge (meq/g) in Different Electrolyte Concentrations at Selected pH Values (Potentiometric Method)

pH	Wet			Oven			P_2O_5			Freeze		
	H_2O	0.01N KCl	0.1N KCl	H_2O	0.01N KCl	0.1N KCl	H_2O	0.01N KCl	0.1N KCl	H_2O	0.01N KCl	0.1N KCl
					Synthesized Minerals							
					Fe hydrous oxide (A)							
3.5	+1.18	+1.44	+1.56	+0.54	+0.80	+1.00	+0.50	+0.86	+1.01	+0.85	+0.95	+1.35
5.0	+0.66	+0.88	+1.07	+0.36	+0.60	+0.78	+0.32	+0.58	+0.74	+0.42	+0.70	+0.82
7.0	+0.26	+0.35	+0.45	+0.21	+0.27	+0.38	+0.20	+0.33	+0.42	+0.14	+0.32	+0.46
8.0	+0.10	+0.16	+0.20	+0.08	+0.14	+0.18	+0.09	+0.15	+0.16	+0.05	+0.13	+0.18
9.5	-0.21	-0.36	-0.50	-0.04	-0.09	-0.11	-0.12	-0.03	-0.12	-0.09	-0.12	-0.30
					Fe hydrous oxide (B)							
3.5	+0.27	+0.34	+0.45	+0.21	-0.28	-0.36	+0.15	+0.20	+0.35	+0.28	+0.33	+0.46
5.0	+0.14	+0.18	+0.29	+0.15	+0.20	+0.26	+0.08	+0.17	+0.30	+0.09	+0.13	+0.25
7.0	+0.06	+0.08	+0.11	+0.04	+0.08	+0.12	+0.04	+0.05	+0.11	+0.03	+0.04	+0.11
8.0	+0.01	+0.02	+0.03	+0.02	+0.03	+0.04	+0.03	+0.04	+0.03	+0.01	+0.02	+0.04
9.5	-0.04	-0.16	-0.50	-0.03	-0.09	-0.28	-0.02	-0.05	-0.39	-0.03	-0.16	-0.38
					Synthesized gibbsite/bayerite							
3.5	+0.34	+0.70	+0.91	+0.15	+0.21	+0.40	+0.21	+0.28	+0.45	+0.28	+0.38	+0.87
5.0	+0.02	+0.04	+0.09	+0.01	+0.05	+0.07	+0.02	+0.04	+0.08	+0.05	+0.06	+0.10
7.0	-0.12	-0.30	-0.38	-0.08	-0.22	-0.26	-0.10	-0.27	-0.24	-0.14	-0.19	+0.28
8.0	-0.20	-0.51	-0.58	-0.17	-0.31	-0.40	-0.18	-0.44	-0.36	-0.18	-0.38	-0.50
9.5	-0.40	-0.66	-0.88	-0.28	-0.48	-0.63	-0.31	-0.51	-0.60	-0.25	-0.59	-0.81

Table 8. Zero Points of Charge (Z.P.C.) for Soils and Synthetic Minerals

Soils	
Akaka	5.0-5.5
Hilo	6.5-7.0
Kawaihae	4.5-5.0
Synthesized Minerals	
Fe hydrous oxide (A)	8.0-8.5
Fe hydrous oxide (B)	8.0-8.5
gibbsite/bayerite	5.5-6.0

values are slightly lower than expected especially for Typic Hydrandepts.

El-Swaify (1976) quoted Z.P.C. values between 3.5-5.0, 6.6-8.7, above 7.7, 6.2, and around 8.0 for kaolin, crystalline iron oxides, crystalline aluminum hydroxides, amorphous silicates, and amorphous-like iron hydrous oxides, respectively, citing Parks (1965, 1967), Atkinson (1967), Breewsma and Lyklema (1973), and Limura (1961). Similar Z.P.C. values for the two Typic Hydrandepts (Figures 7 and 8) were reported by El-Swaify and Sayegh (1975) and by Tama (1975) for Akaka and Hilo, respectively. It is interesting to note that neither drying nor hydrogen peroxide treatments in this study affected the Z.P.C. values. An examination of the magnitudes of net charges (positive and negative) for the soils and synthesized minerals showed both to be increased by increasing electrolyte concentration. Higher dependence of net charges on concentration are noted for Typic Hydrandepts and Fe hydrous oxide (A) than for Kawaihae and Fe hydrous oxide (B), respectively. As explained by El-Swaify and Sayegh (1975), this is due to differences in potential sites available for acquiring charges over an extended surface area (Table 10). Again, there were no significant changes in charge characteristics due to peroxidation. However, various drying treatments altered net charges tremendously. Tweneboah (1967) as well as Deshpande et al.

(1964), reported that normal peroxidation of the soil which had 7.4% organic carbon and positive charge of 1.85 meq/100g at pH 3.0, reduced the latter by only 0.04 meq/100g, whereas, peroxidation at alkaline condition increased positive charge to about 4.5 times the original values. Two reasons were proposed for positive charge decrease in some soils upon normal peroxidation: (1) that some positive charge sites are removed by dissolution of aluminum and iron due to oxalates formation during oxidation (Farmer and Mitchell, 1963), or (2) that positive sites may react with oxalates produced during oxidation to form insoluble complexes (Farmer and Mitchell, 1963, and Oades and Townsend, 1963). But at high pH, positive charges are suppressed and the sites are not capable of complexing oxalates.

Table 7 presents net charge values for various drying treatments at selected pH values. It is clearly evident that net charges (positive and negative) at all pH values were decreased by any of the drying treatments. This decrease was generally in the order: oven drying>P_2O_5 drying>freeze drying. Little change was noted in Kawaihae soil, Fe hydrous oxide (B), and in gibbsite/bayerite.

In other words, soils in wet areas (which had not been subjected to natural drying cycles) were most prominently affected by drying than soils in dry areas. Also, the soils containing amorphous like minerals and amorphous like mineral were more

affected by drying.

Kanehiro and Sherman (1956) reported significant C.E.C. reductions (74.7%) due to dehydration induced by sun-drying for 100 days and in an oven at 105°C for 7 days for Typic Hydrandepts and some other soils. For soils from dry and moderately wet areas, C.E.C. increased significantly upon rehydration. Such was not the case for soils from wet areas. Net charge alteration upon drying observed in this study could be considered as a direct reason for these apparent decreases in C.E.C. by dehydration. The information in Figures 7-9 and Table 7 show that such alterations are not confined to pH 7 as is the case for C.E.C. values.

C. Observation of Physical Properties

1. Particle size analysis

To determine conditions favoring optimum dispersion for particle size distribution analysis, some preliminary experiments were conducted. Figure 13 shows effectiveness of different shaking periods in inducing dispersion. It is noted that the rate of clay release changes more rapidly during the initial 20 minutes than after. However, the two P_2O_5 dried Typic Hydrandepts still underwent significant increases in clay release by shaking for longer periods of time. For convenience, however, the 20 minute shaking period was chosen for this particular experiment.

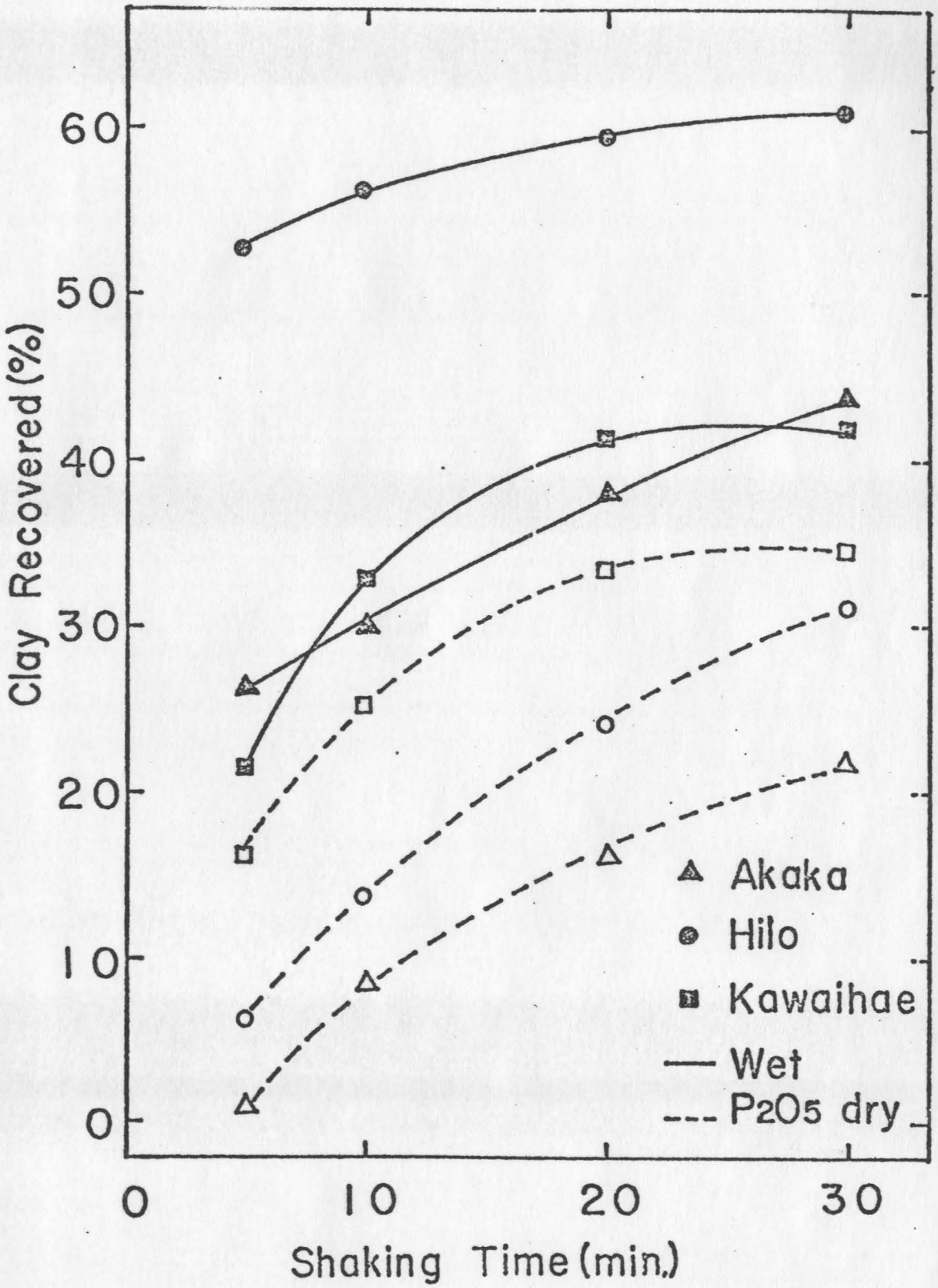


Figure 13. Effects of shaking time on aggregate breakdown for natural and dried soils.

To further refine the method, a determination was made of the effective water content for dispersion. Figure 14 shows that maximum dispersion was achieved at soil:water ratios of 1:4, 1:6, and 1:8 for original Kawaihae, Hilo, and Akaka soils, respectively. This result coincided well with respective surface areas of the soils (Table 10). To explain this observation, it is important to note that maximum dispersion is favored both by the physical breakdown and subsequent release of constituent particles during the shaking process and also by the need to achieve a critical interparticle distance for maintaining colloidal stability. Therefore, the interaggregate frictional forces and water film thickness around particles would be expected to play primary roles for clay release. At low water content, water film thickness would be insufficient to provide interparticle separation completely even though frictional force may be large enough to break down soil aggregates. At high water content, there is probably insufficient friction between aggregates to cause effective mutual breakdown. It is also expected that the optimum soil:water ratio would be affected by the speed of shaking, type of shaking, and volume of container. Figures 15 and 16 show particle size changes upon drying using a shaking period of 20 minutes and soil:water ratios of 1:4 for Kawaihae and dried soils, 1:6 for undried Hilo, and 1:8 for undried Akaka and synthetic minerals. It is noted that except for the Kawaihae soil, a significant

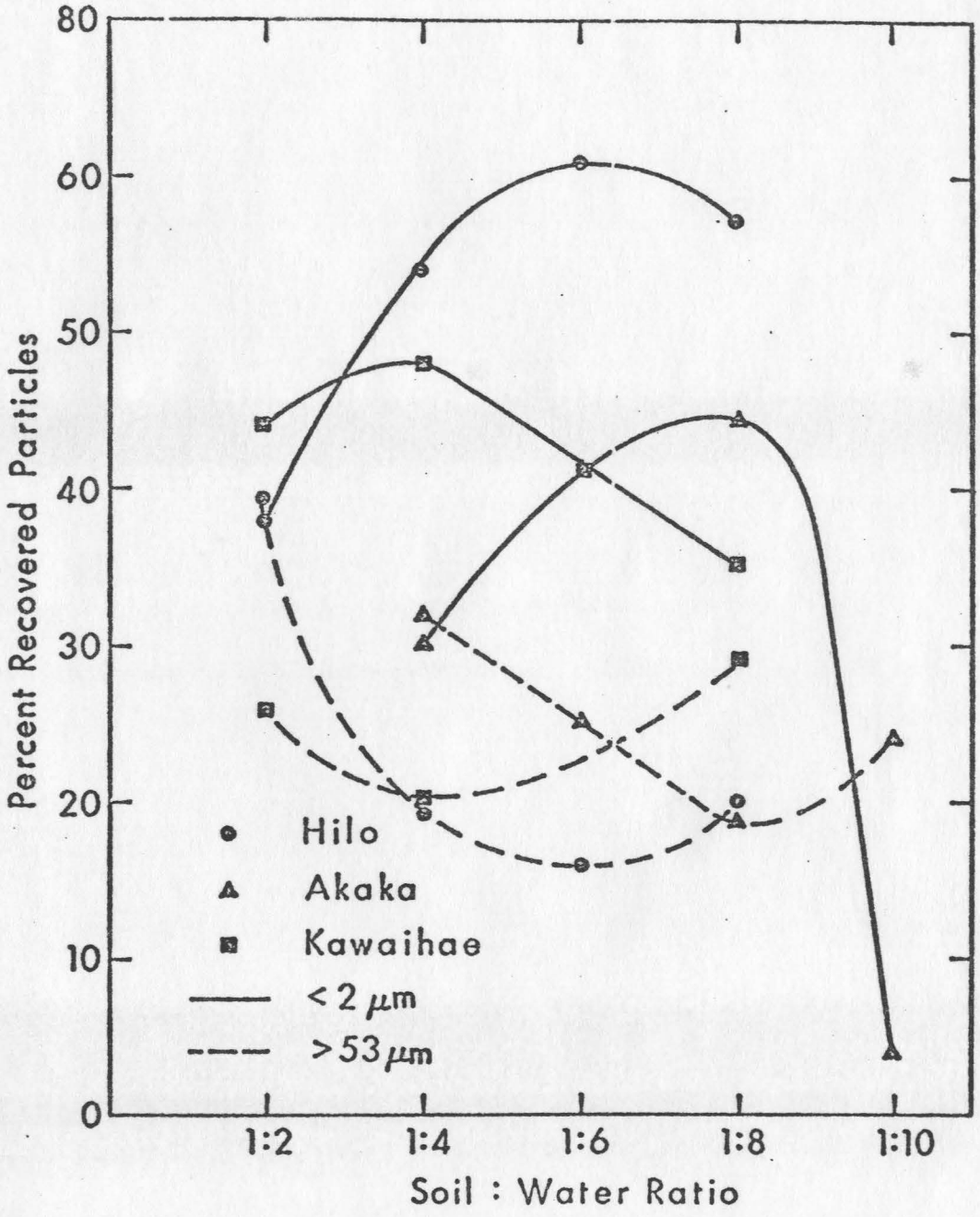


Figure 14. Effects of soil:water ratio on aggregate breakdown of soils.

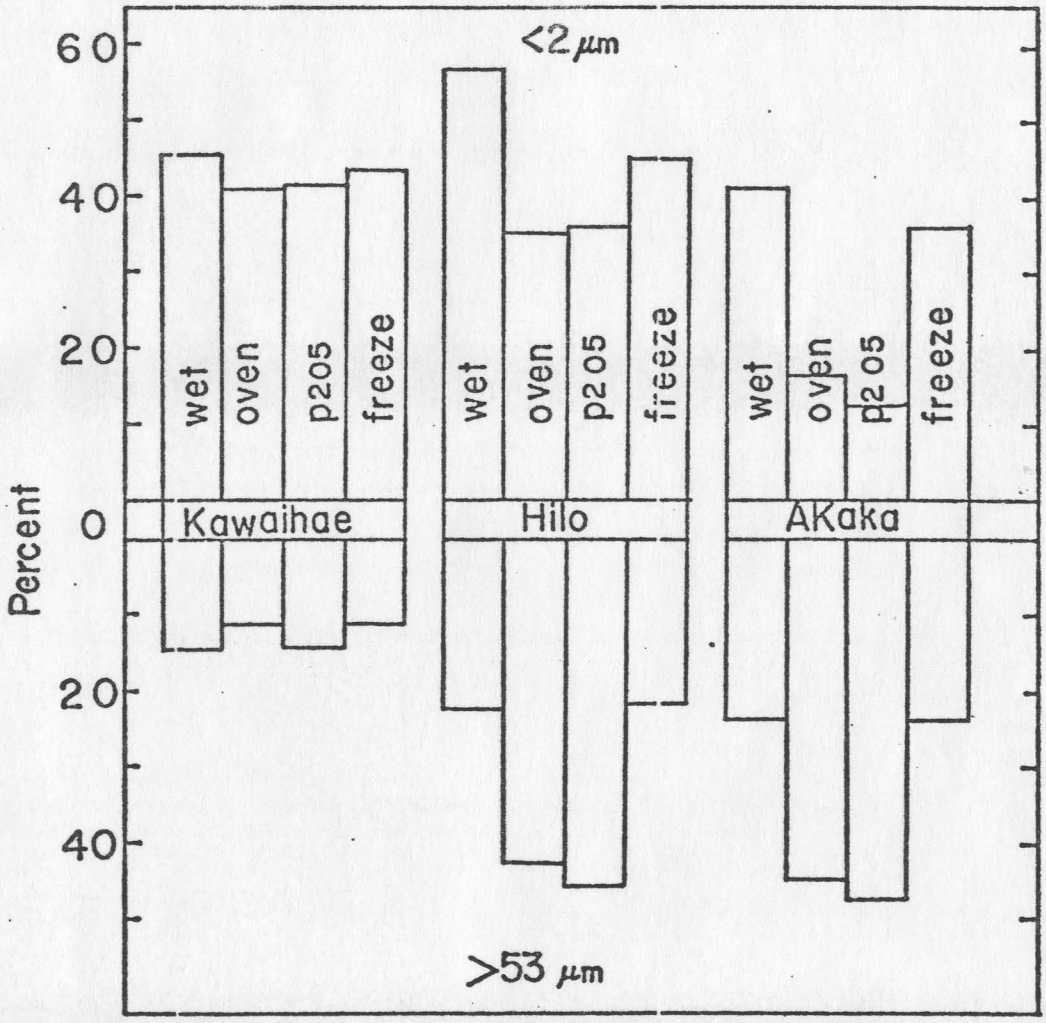


Figure 15. Particle size distribution for soils.

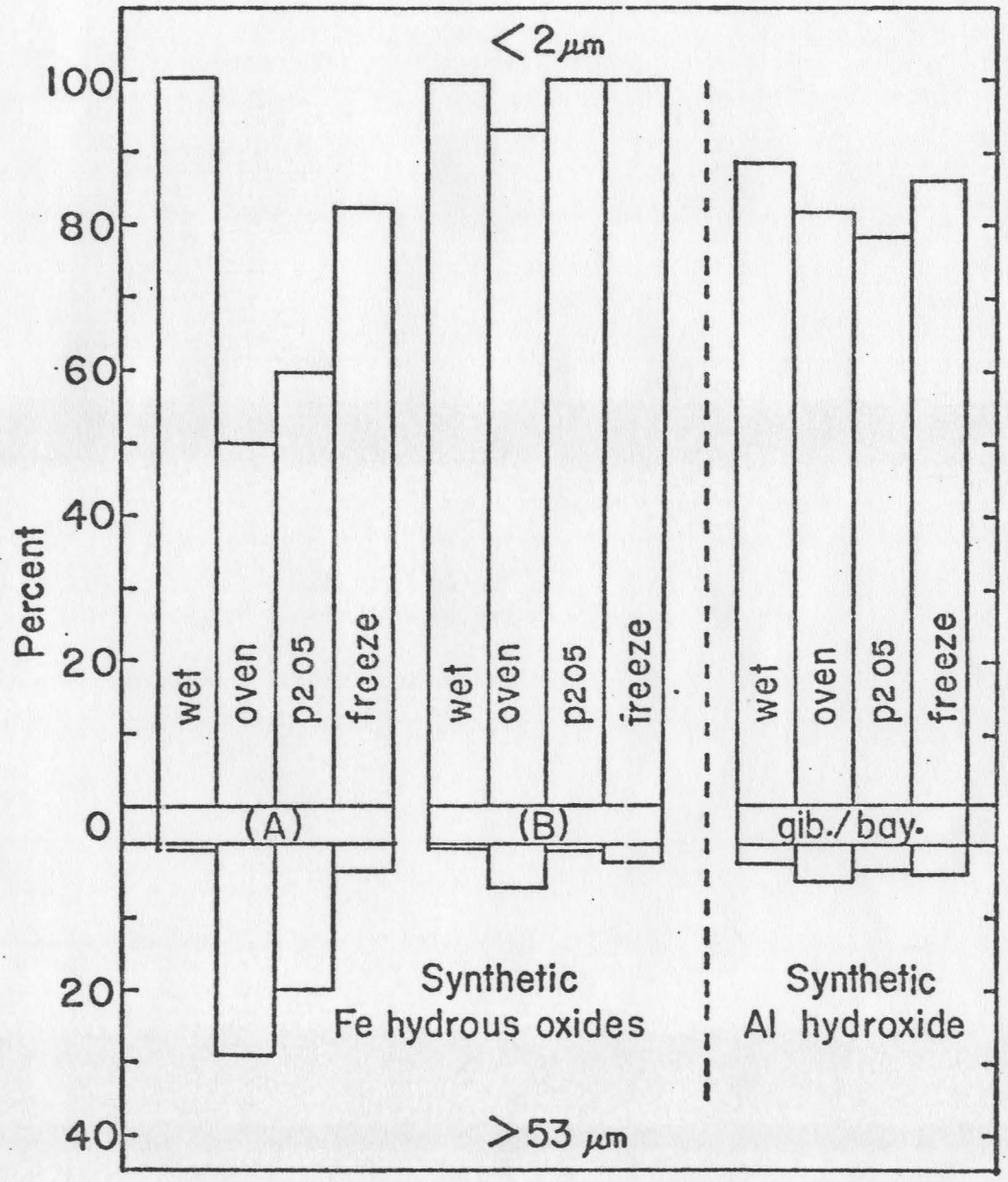


Figure 16. Particle size distribution for synthetic minerals.

decrease in released <2 μm particles occurs due to any drying treatment. Conversely, more particles >53μm in size were detected in dried samples. It is important to note that release of <2μm particles is a better indication of dispersion effectiveness than is the content of >53 μm particles since much of the latter could be a true sand fraction. For drying effects, it is clear that most of the initial <2μm particles were agglomerated by drying in >53μm sized ones. Drying treatments affected this change in the order: oven dry>P_2O_5 dry>freeze dry. H_2O_2 treatment somewhat reduced the drastic effects of drying indicating that the cementing role of organic matter is important for enhancing interparticle bonding. This is one indication that drying effects on the behavior of Typic Hydrandepts are more physical than mineralogical in nature. The additional cementing role of very fine constituents is noted from comparing drying effects on Fe hydrous oxide (A) and Fe hydrous oxide (B) (Figure 16). The first is more significantly affected by drying than the second as far as release of <2μm particles is concerned. This supports the hypothesis that physical cementation is responsible for interparticle bonding upon drying. The more significant effects of drying on Akaka than Hilo soil would indicate that the first has more effecting cementing organic or inorganic agents than does the second.

2. Water retention measurement

As all the previous results (net change and particle size distribution), dehydration treatments altered water retention capacity tremendously for all except the Kawaihae soil (Table 9). Typic Hydrandepts and Fe hydrous oxide (A) were more affected than Fe hydrous oxide (B). The effects of dehydration and of hydrogen peroxide treatment agree exactly with previous observations on net charge and particle size distribution. However, the effect of hydrogen peroxide treatment was better manifested here, even in Kawaihae soil which has only 2.0% organic matter. Also, the effect of freeze drying was closer to the effects of other drying treatments here as compared with previous observations, although the order of treatments is not changed. The hydrogen peroxide treatment effects may be explained by the fact that organic matter has a dual effect on water retention, i.e., by holding its own molecular water groups as well as changing the water holding matrix of soil. The latter effects both the swelling and capillary mechanisms, particularly the first, of water retention (El-Swaify and Lim, 1976, and Tsuji, Watanabe, and Sakai, 1975). Constituents released by organic matter decomposition may also have an effect on water retention. Therefore, even though freeze drying was somewhat distinguishable from other drying treatments, the loss of swelling capacity by any drying history overwhelmed the noted effects.

Table 9. Water Retention (g/g) at 10 and 50 cm Tensions

	Wet		Freeze		P_2O_5		Oven	
	10cm	50cm	10cm	50cm	10cm	50cm	10cm	50cm
			Akaka Soil					
untreated	1.088	0.912	0.509	0.488	0.489	0.410	0.374	0.316
H_2O_2 treated	1.163	1.140	0.396	0.321	0.368	0.331	0.322	0.302
H_2O_2 control	1.357	1.295	0.467	0.444	0.397	0.378	0.335	0.318
			Hilo Soil					
untreated	1.016	0.898	0.393	0.393	0.391	0.374	0.334	0.327
H_2O_2 treated	1.233	1.230	0.362	0.351	0.334	0.330	0.338	0.309
H_2O_2 control	1.342	1.325	0.404	0.373	0.365	0.349	0.312	0.290
			Kawaihae Soil					
untreated	0.273	0.258	0.334	0.289	0.306	0.304	0.286	0.283
H_2O_2 treated	0.266	0.238	0.291	0.278	0.310	0.279	0.280	0.270
H_2O_2 control	0.338	0.286	0.307	0.285	0.300	0.287	0.276	0.262
			Synthesized Fe hydrous oxides					
Fe-hydrous oxide (A)	5.029	4.981	0.474	0.468	0.434	0.431	0.445	0.434
Fe-hydrous oxide (B)	2.355	2.345	0.792	0.723	0.814	0.638	0.712	0.641

Table 9 (Continued). Water Retention (g/g) at 10 and 50 cm Tensions

	Wet		Freeze		P_2O_5		Oven	
	10cm	50cm	10cm	50cm	10cm	50cm	10cm	50cm
commercial goethite (air dried)			0.0908		0.0847			
			Synthesized Al-hydroxide					
Gibbsite/bayerite	0.743	0.743	0.755	0.670	0.771	0.649	0.433	0.355

Furthermore, the well known hysteresis which occurs in pore spaces of dried soils entrapping air (Baver, 1956) has possibly influenced water retention by the soils subjected to drying. This problem was minimized by starting the retention experiments from the wet end in every instance.

Tsuji et al. (1975) mentioned that Akaka soil shrank in volume by as much as 50% by changing from saturation to a suction of 300 cm. El-Swaify and Lim (1976) indicated that shrinkage limit for Hilo soil is 45-50% and estimated a mean particle separation of 45Å at that moisture content based on the measured surface area of 150-200 m^2/g. It is also clearly noted that a difference existed between the control treatment used as a basis for H_2O_2 effects and the untreated (original) soil. The strong puddling employed during the stirring of the first caused a more effective dispersion of aggregates.

3. Specific surface measurements

Surface areas were obtained by applying the B.E.T. equation to water vapor adsorption isotherms constructed at various relative humidities.

Table 10 shows that Typic Hydrandepts, by virtue of strong aggregation upon drying caused by their large contents of cementing agents, underwent drastic decrease in surface area. Likewise, Fe hydrous oxide (A) exhibited as larger surface

Table 10. Specific Surface (m^2/g) by H_2O Vapor Adsorption

Treatments	Wet	Oven	P_2O_5	Freeze
		Akaka		
original	289	141	166	168
H_2O_2 treatment	239	127	130	134
H_2O_2 control	272	124	161	171
		Hilo		
original	268	139	146	149
H_2O_2 treatment	223	118	129	131
H_2O_2 control	260	122	136	143
		Kawaihae		
original	93	87	94	98
H_2O_2 treatment	86	86	83	88
H_2O_2 control	86	84	85	87
		Fe hydrous oxides		
Fe hydrous oxide (A)	298	239	263	285
Fe hydrous oxide (B)	38	40	41	40
commercial goethite (air dried)		3		
		Al hydroxides		
Gibbsite/bayerite	38	36	35	38

area reduction upon drying than both Fe hydrous oxide (B) and Al hydroxide minerals. However, changes in the two Typic Hydrandepts were more drastic than in the Fe hydrous oxide (A), reflecting organic matter contribution. Removal of organic matter resulted in less relative reduction in surface area due to drying. El-Swaify and Emerson (1975) precipitated Fe- and Al-hydroxides alone and in the presence of various clay minerals systems using the same precipitation methods of this study. They found that Fe-hydroxides precipitated in presence of clay minerals consisted of particles about 40Å in diameter and generally x-ray amorphous rather than the acicular goethite crystals that precipitated in the absence of clays. This means that the goethite synthesized in this way could have surface area between 238.3 m^2/g (assuming cylinder shape) and 350.5 m^2/g (assuming spherical particles) when goethite particle density of 4.28 g/cm^3 is assumed. The authors also showed that the B.E.T. N_2 surface areas of precipitated goethite and bayerite were 259 and 57 m^2/g, respectively. But El-Swaify and Lim (1976) observed, by electron-microscopic examination, that Fe constituents in surface Hilo soil appeared as needles made of beads which are spherical in form. For P_2O_5 and freeze dried Hilo soil, they calculated B.E.T. surface areas of around 150 m^2/g by water vapor adsorption. Based on the water adsorption data of Wadsworth (1944), Quirk (1955) reported a surface area of

165 m^2/g for an unidentified soil from the Hilo coast.

In addition to the organic matter contribution discussed above, the larger reduction due to drying in Hilo and Akaka soil surface area than in Fe hydrous oxide (A) may be due to differences in particle configurations. In the pure Fe hydrous oxides particles are expected to be of more uniform size and shape and subsequently would have a relatively small chance of producing a tightly packed system upon drying. On the other hand, the soils are made up of particles of many shapes and sizes (Lai and Swindale, 1967; Chan, 1972; and El-Swaify and Lim, 1976) which, due to overlaps and mutual incorporation, allow more intimate contacts upon drying.

4. Colloidal stability measurement

Figures 17-22 show the relationship between extractable clay and pH for the soils before and after P_2O_5 drying. Only the Hilo soil exhibits a symmetrical diagram with a pivot at the Z.P.C. When not subjected to drying, the Akaka soil is slightly dispersed below the Z.P.C. but, as is the case for the Kawaihae soil, the most effective stability range lies above the Z.P.C. P_2O_5 drying does not change the shape of the colloidal stability but there is some reduction in clay stability for both the Akaka and Hilo soils. On the other hand, appropriate pH adjustment helped effective breakdown of aggregates formed by

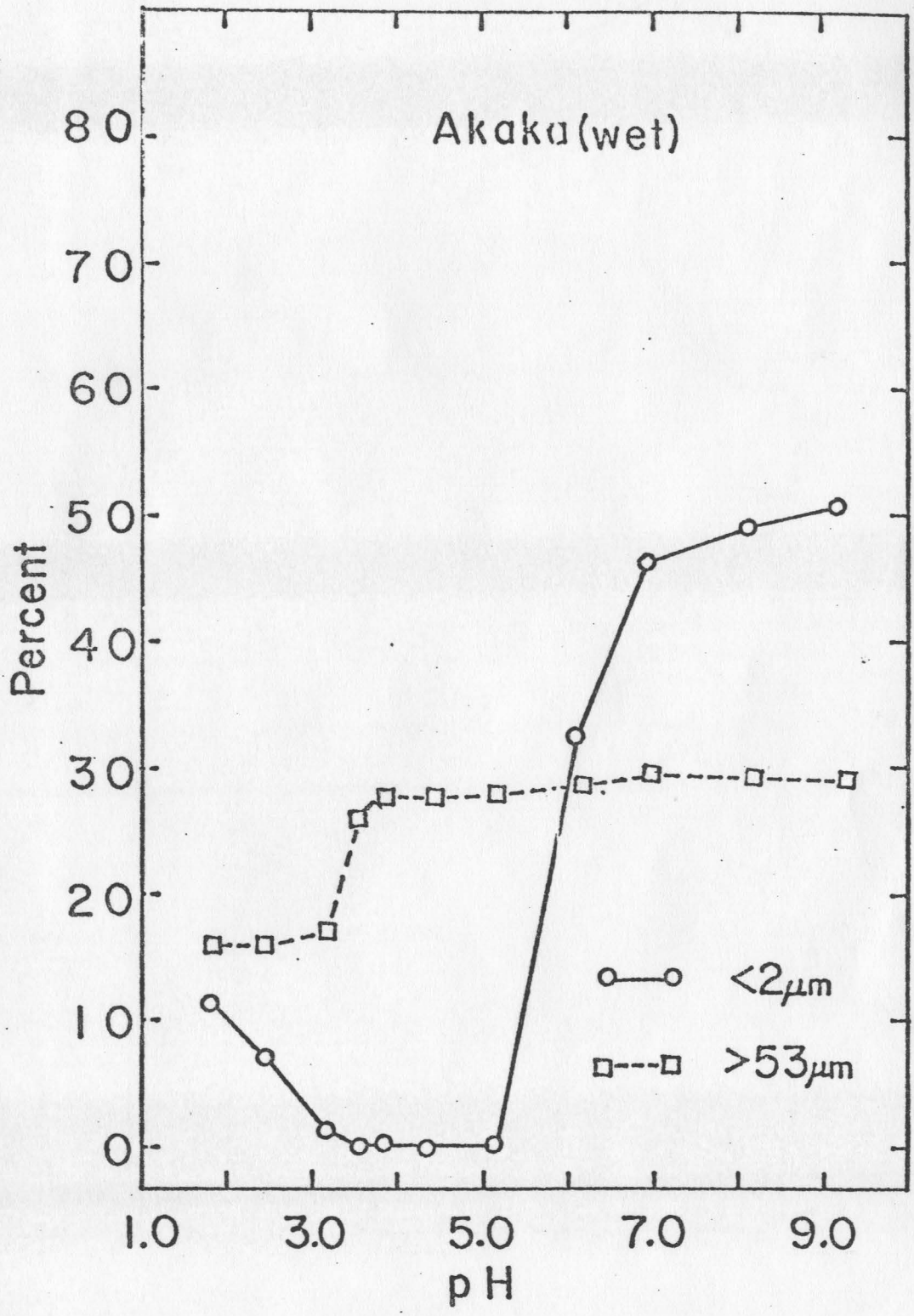


Figure 17. Colloidal stability of untreated Akaka soil at different pH values.

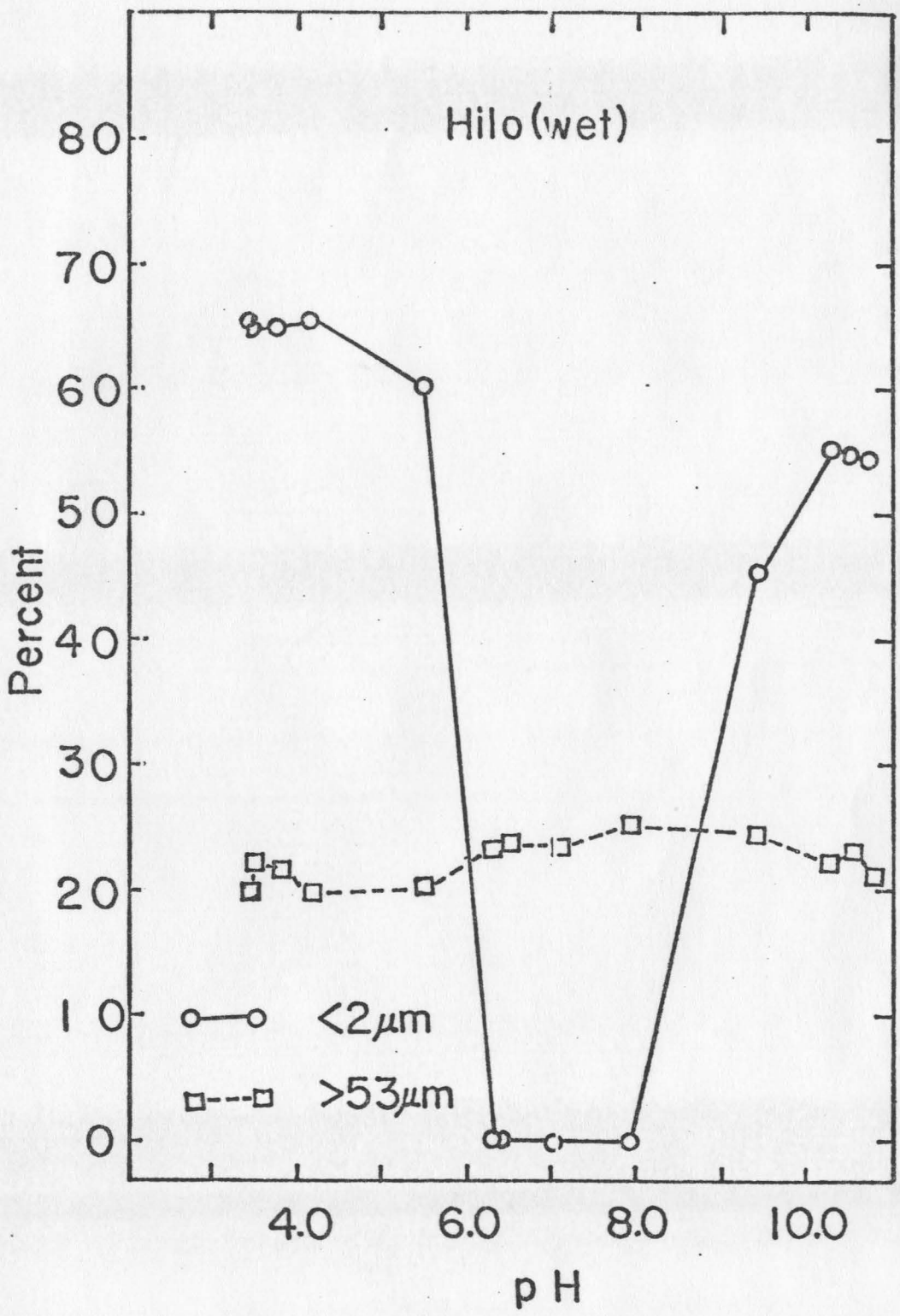


Figure 18. Colloidal stability of untreated Hilo soil at different pH values.

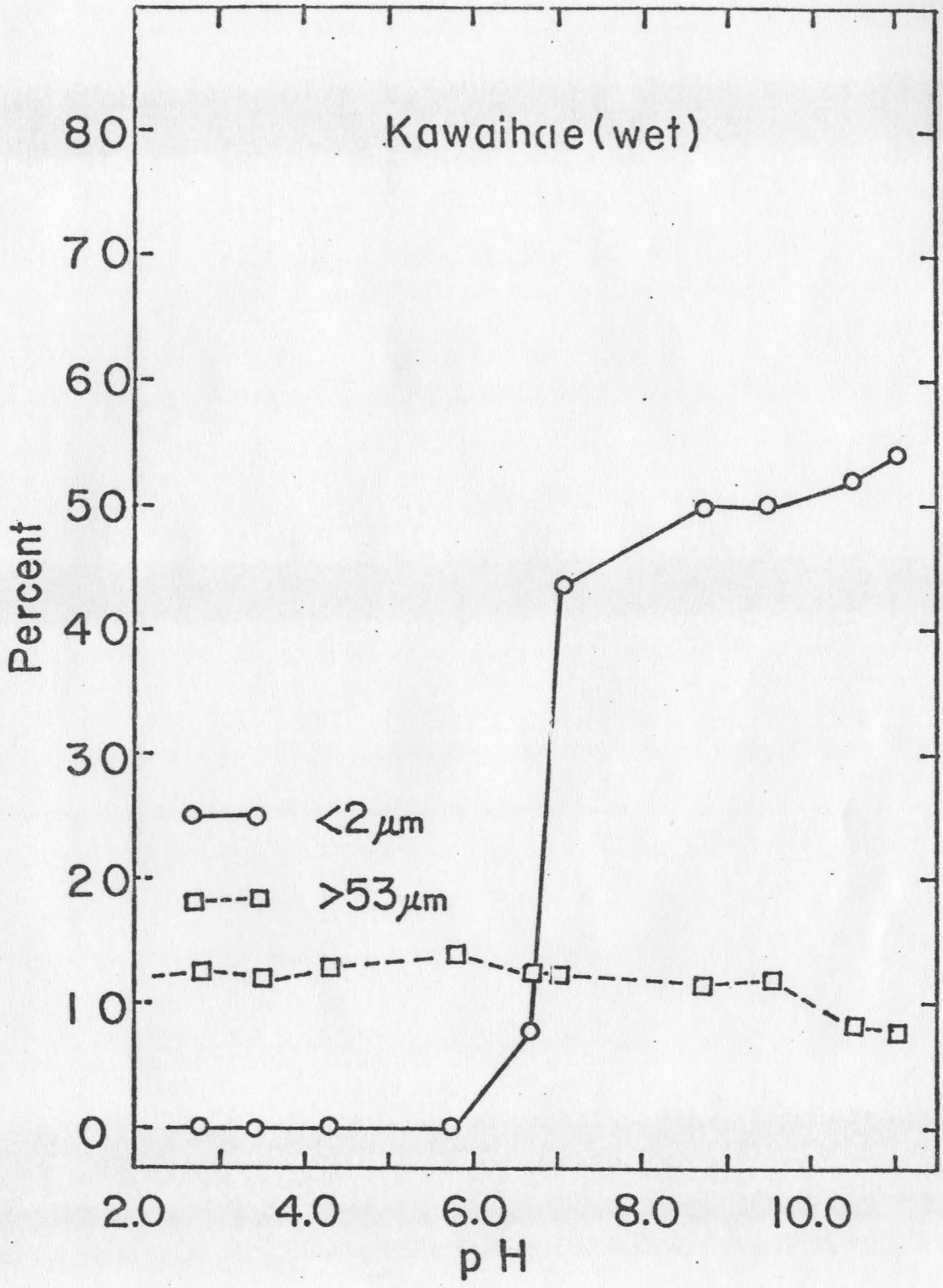


Figure 19. Colloidal stability of untreated Kawaihae soil at different pH values.

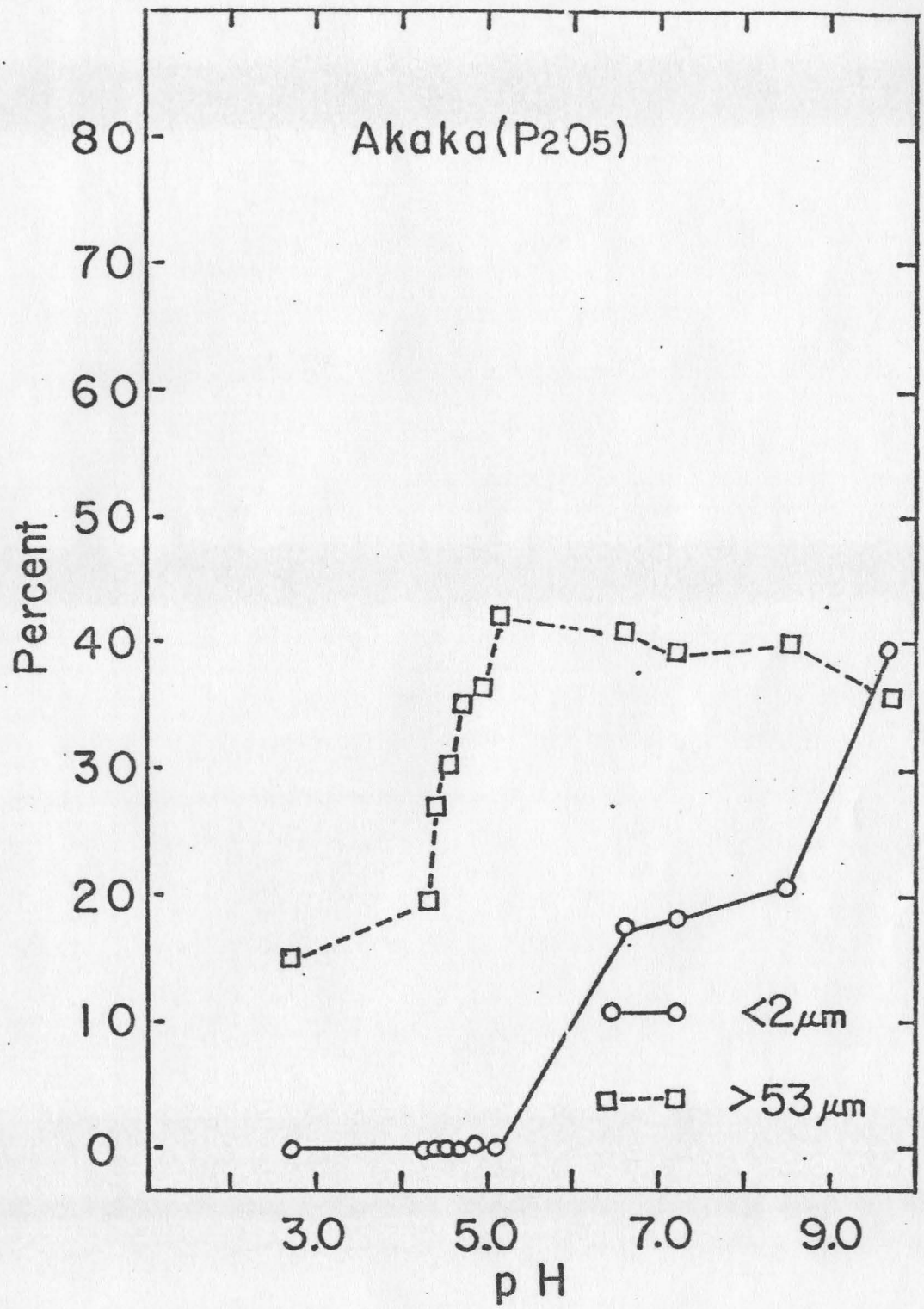


Figure 20. Colloidal stability of Akaka soil at different pH values after P_2O_5 drying.

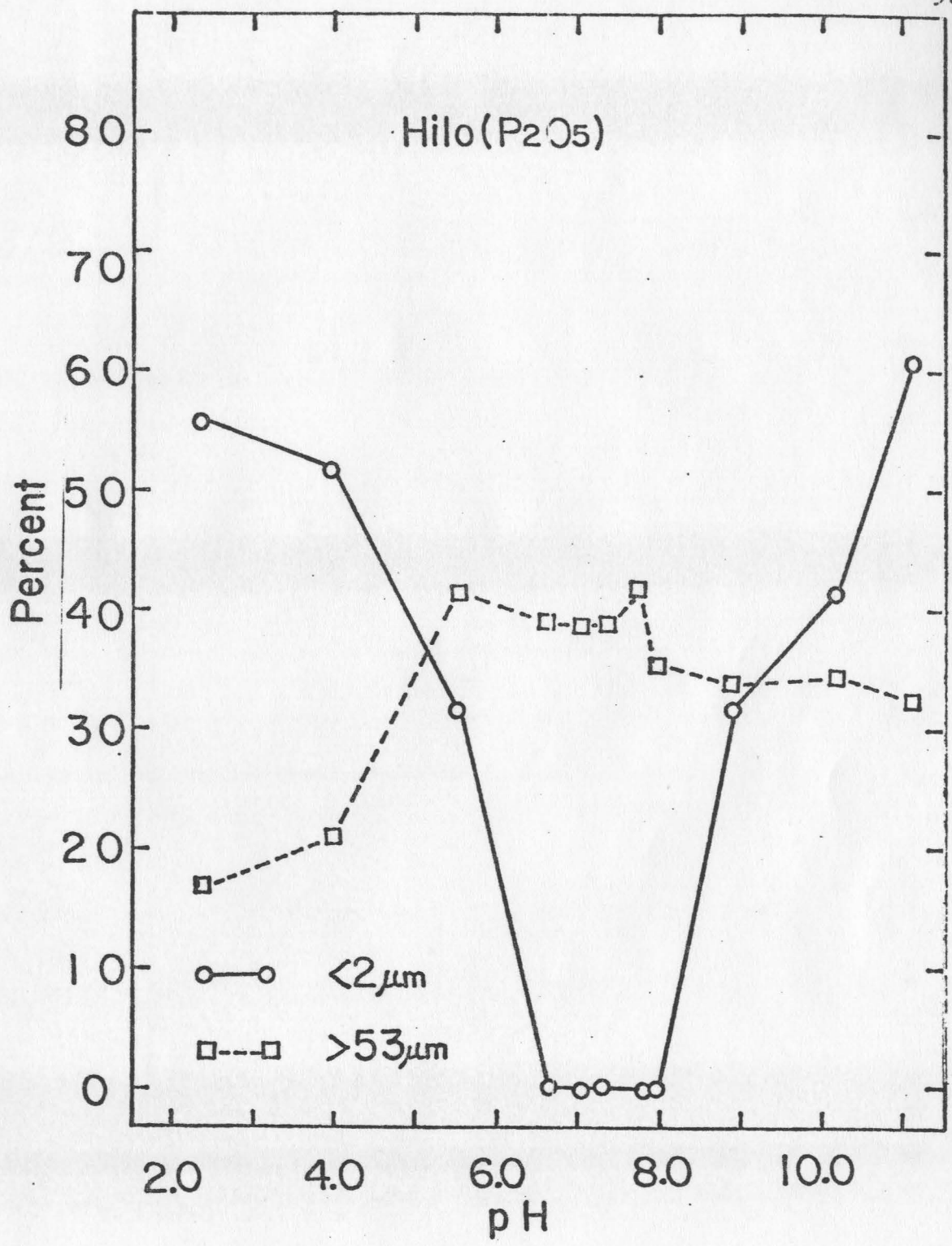


Figure 21. Colloidal stability of Hilo soil at different pH values after P_2O_5 drying.

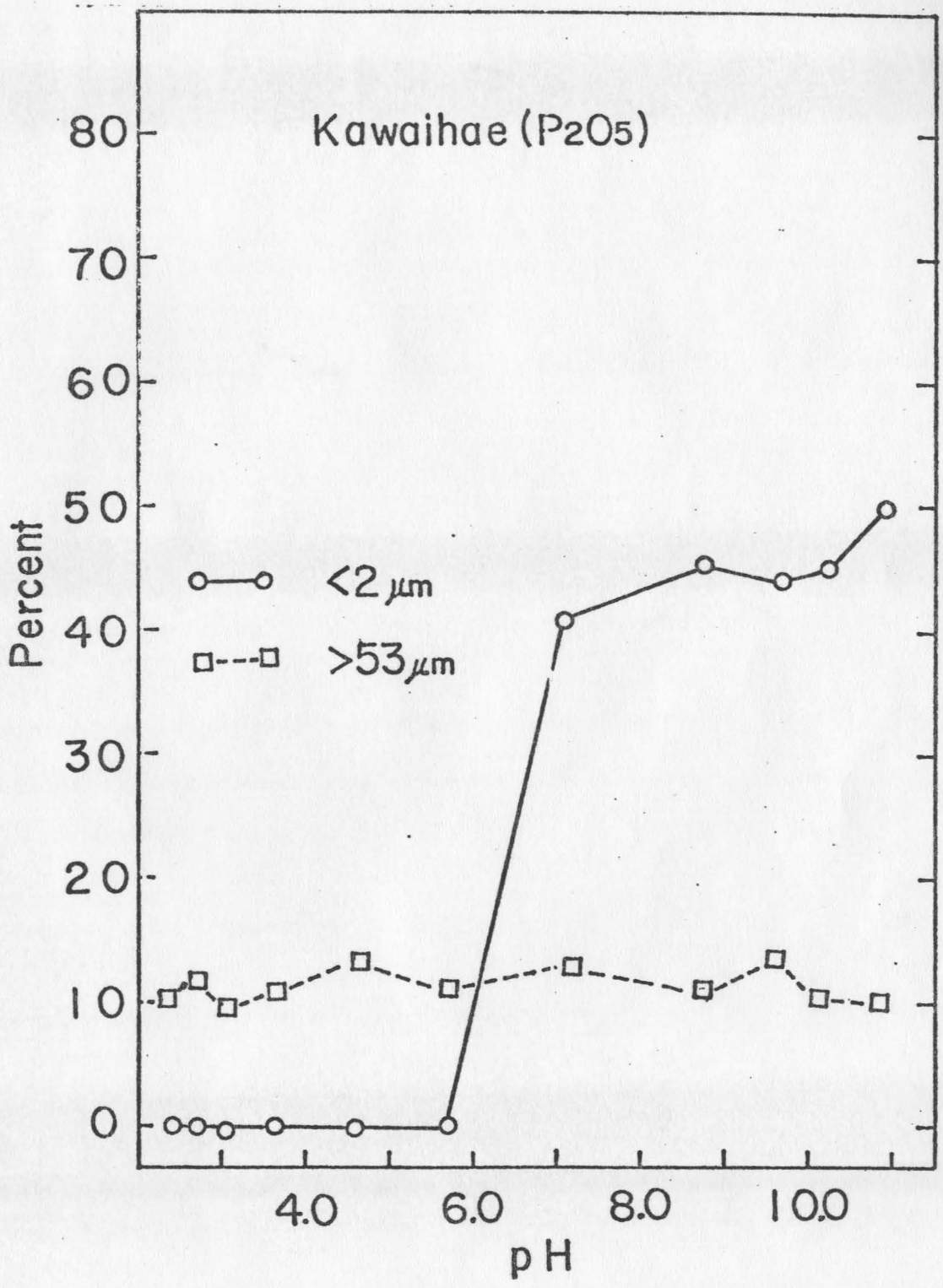


Figure 22. Colloidal stability of Kawaihae soil at different pH values after P_2O_5 drying.

the drying treatment. For the Hilo soil, lowering the pH was more effective for restoring original mechanical composition. However, raising the pH is the better alternative for Akaka and Kawaihae soils. These results are predictable primarily from Z.P.C.'s of the soils (Table 8) and from magnitudes of net charge observed for the various treatments (Table 7). An analysis of variation in interparticle attractions and repulsions near the Z.P.C. was given by El-Swaify (1976). It may be pointed out that there is some discrepancy between predicted and observed stabilities. Recall equation (7) and the following equation:

$$\sigma = - \frac{DK}{4\pi}\left(0.059(\text{pH}-\text{Z.P.C.})\right) \qquad (12)$$

in which all terms were previously defined. The first equation (7) shows that surface charge (σ either positive or negative) is developed for colloids with constant surface potential by adjusting pH away from Z.P.C. at which maximum mutual flocculation occurs, and by increasing electrolyte concentration. This ideal situation is true only in the absence of specific interaction between the colloidal surface and counter ions. The second equation predicts that repulsion energy (V_R) decays exponentially with interparticle separation, and the rate of decay is determined by electrolyte concentration and counter ion valency. Its reciprocal, $1/\kappa$, is a measure of double layer thickness and is reduced by increasing electrolyte concentration thus giving rise to the

manifestation of London-van der Waal's attractions (V_A, see equation 11). Accordingly, colloidal stability will be reduced. This is an apparent contradiction to predictions based on charge development alone. In reality, colloidal stability depends both upon charge development and the compressibility of effective thickness of the diffuse double layer. The latter may be due to presence of indifferent electrolytes or appropriate concentrations of specifically adsorbed ions. Thus, the slight reduction in stability noted for the Hilo soil above pH 10.2 and the inability to stabilize Akaka and Kawaihae soils at very low pH values, both may be due to the presence of excess electrolyte which in these cases were NaOH or HCl. Amphoteric colloids with very low Z.P.C. (such as Kawaihae and Akaka soils) are difficult to stabilize by decreasing the pH on the acid side of the Z.P.C. Similarly, those with high Z.P.C. are difficult to stabilize above the Z.P.C. El-Swaify (1976) for this reason, was unable to obtain effective stabilization of gibbsite and bayerite above their Z.P.C.'s. The small amount of repulsive forces which caused the slight dispersion of the undried Akaka soil below pH 4 (Figure 17) was effectively overcome by additional interparticle bonds caused by drying (Figure 20). Also, the magnitude of charges developed by this soil at low pH were by drying (Table 7). In contrast, the Hilo soil has a Z.P.C. near neutrality (around pH 6.5). Consequently, it is equally possible for this

soil to develop sufficient charges to sustain colloidal stability both below and above the Z.P.C. thus producing a somewhat symmetrical stability diagram (Figure 18). In further support of these observations, Tama (1975) failed to stabilize the Molokai (oxisol) and Waikane (Ultisol) soils below their Z.P.C. values which he reported as 2.5-2.9 and 3.0-4.0 for the two soils, respectively. Also, El-Swaify (1976) was able to obtain symmetrical stability diagrams only for goethite and a few mixtures of Al- or Fe-hydroxides and kaolinite, illite, and kaolinite-illite.

Based on the stability diagrams for the three soils, it may be predicted that effective restoration of original soil conditions may be best achieved at pH values of 8-9 and 3-4 for the Akaka and Hilo soils, respectively.

SUMMARY AND CONCLUSIONS

The effects of drying by various well-defined methods on water retention, structural charge, and surface characteristics of two Typic Hydrandepts and one Camborthid were investigated. The roles played by various cementing constituents in determining the effects of drying were investigated both by selective extraction (using H_2O_2 to remove organic matter) and by synthetic techniques (to determine the effects of present Fe-hydrous oxides and Al-hydroxide). Chemical conditions favoring restoration of original soil properties after drying were also investigated. From the results obtained with these experiments, it was concluded that:

1. The high field water contents of Typic Hydrandepts are accounted for by their large surface areas which approach 250 m^2/g. Amorphous or gel like fine crystalline constituents are responsible for these large areas as they account for 60-65% and 75-80% of the total constituents in Hilo and Akaka soils, respectively.
2. Comparison between water losses by freeze-drying, P_2O_5-drying, and oven drying at 105°C showed that the first two methods are preferable for determination of soil water contents of Typic Hydrandepts. Oven drying caused additional losses of some structural water which cannot be considered active in transport phenomena or

available to growing plants.

3. The occurrence of mineralogical transformations upon drying of Typic Hydrandepts at ordinary temperatures could not be confirmed in this study. Decreased x-ray attenuation in samples not subjected to drying was probably due to dilution of mineral constituents by the water present. Drying at elevated temperatures, on the other hand, may be considered a cause for mineralogical changes as indicated by loss of structural water. All drying treatments did result in significant changes in soil physical properties.

4. Changes in physical properties due to the three well-delined dehydration treatments included increases in aggregate sizes and amounts and reductions of specific surface, water retention, and measureable net charges. These changes were in the order: oven drying>P_2O_5 drying>freeze drying. It was concluded that freeze drying was the best alternative studied here for preserving natural soil structural conditions. A preliminary visual examination of a sample exposed to critical point drying indicated that this method may be even more superior.

5. The presence of effective cementing constituents is largely responsible for changes in the properties of

Typic Hydrandepts upon drying. This was evidenced, on the one hand, by less drastic changes due to drying after organic matter was decomposed. On the other hand, it was shown on synthesized Fe hydrous oxide (A) that the higher contents of amorphous like fine crystalline constituents resulted in more pronounced effects of drying. Large crystalline goethite and Al-hydroxide (gibbsite/bayerite) underwent little change in properties when dried at ordinary temperatures. Furthermore, the presence of high amounts of dithionite- or oxalate-extractable Fe and Al in the soils and synthesized minerals was related to a high tendency for drastic changes in properties to occur upon drying. The oxalate-extracted Fe and Al appeared to be more related to the soil content of amorphous or gel like crystalline materials while the dithionite was a less discriminating extractant. Dissolution of both reagents was reduced by all drying treatments except for freeze drying.

6. Proper selection of physical methods and chemical variables is important for aiding the rehydration process of dried Typic Hydrandepts. Nearly 90% and 79% of the original contents of clay-sized particles were recovered from Hilo and Akaka soils, respectively, when vigorous shaking was applied for 20 minutes to samples to which

optimum amounts of solutions were added and when the final pH levels were adjusted to favor maximum dispersion. Shaking for longer periods of time, particularly of samples subjected to the least drastic drying treatments, is expected to produce near complete recovery of initial soil properties.

APPENDIX I

Zero Point of Charge (Z.P.C.)

Treatments	Wet	Oven	P_2O_5	Freeze
		Akaka Soil		
original	5.2-5.5	5.5-5.8	5.6-5.9	5.2-5.5
H_2O_2 treatment	5.5-5.7	5.6-5.8	5.7-5.9	5.3-5.6
H_2O_2 control	5.7-5.9	5.5-5.8	5.2-5.5	5.0-5.2
		Hilo Soil		
original	6.2-6.5	6.5-6.7	6.5-6.7	6.0-6.3
H_2O_2 treatment	6.5-6.7	6.0-6.2	5.8-6.0	6.0-6.2
H_2O_2 control	5.8-6.3	5.8-6.1	6.0-6.3	5.8-6.3
		Kawaihae Soil		
original	4.0-5.0	4.0-5.0	4.0-5.0	4.0-5.0
H_2O_2 treatment	4.0-5.0	4.0-5.0	4.0-5.0	4.0-5.0
H_2O_2 control	4.0-5.0	4.0-5.0	4.0-5.0	4.0-5.0
		Fe hydrous oxides		
Fe hydrous oxide (A)	8.0-8.3	8.7-8.9	8.4-8.6	8.1-8.3
Fe hydrous oxide (B)	8.7-8.9	8.4-8.6	8.9-9.1	8.6-8.8
		Al hydroxide		
Gibbsite/bayerite	5.5-6.5	5.5-6.5	5.5-6.5	5.5-6.5

APPENDIX II

Change of Particle Size Distribution Upon Various Drying Treatments

Particle Size	Wet	Oven	P_2O_5	Freeze
		Akaka Soil		
		Original (untreated) soil		
less than 2 μm	41.5	16.8	12.8	36.2
2μm-53 μm	34.6	40.2	40.1	40.1
larger than 53 μm	23.7	45.0	47.5	24.9
sum	99.8	102.0	100.4	101.2
		H_2O_2 treated soil		
less than 2 μm	39.4	15.0	19.0	37.7
2μm-53 μm	45.7	42.7	38.1	50.0
larger than 53 μm	13.8	42.5	44.4	12.6
sum	98.9	100.2	101.5	100.3
		H_2O_2 control		
less than 2μm	44.4	18.8	19.0	44.7
2μm-53 μm	40.3	29.9	33.1	42.9
larger than 53 μm	17.2	50.4	48.6	14.4
sum	101.9	99.1	100.7	102.0

APPENDIX II (Continued)

Change of Particle Size Distribution
Upon Various Drying Treatments

Particle Size	Wet	Oven	P_2O_5	Freeze
		Hilo Soil		
		Original (untreated) soil		
less than 2 μm	56.7	34.9	36.7	45.0
2 μm - 53 μm	25.3	23.8	17.7	34.1
larger than 53 μm	18.7	42.7	45.7	21.8
sum	100.7	101.4	100.1	100.9
		H_2O_2 treated soil		
less than 2 μm	58.0	35.5	38.0	43.9
2 μm - 53 μm	29.0	26.8	24.2	38.5
larger than 53 μm	15.1	39.5	37.9	18.2
sum	102.1	101.8	100.1	100.6
		H_2O_2 control		
less than 2 μm	55.8	38.5	37.9	44.6
2 μm - 53 μm	24.7	21.4	22.4	36.0
larger than 53 μm	20.1	41.5	41.3	19.7
sum	100.6	101.4	101.6	100.3

APPENDIX II (Continued)

Change of Particle Size Distribution Upon Various Drying Treatments

Particle Size	Wet	Oven	P_2O_5	Freeze
		Kawaihae Soil		
		Original (untreated) soil		
less than 2μm	45.7	40.9	41.4	43.5
2μm-53μm	40.3	46.9	43.2	46.3
larger than 53 μm	14.8	11.4	14.8	11.4
sum	100.8	99.0	99.4	101.2
		H_2O_2 treated soil		
less than 2μm	44.1	44.4	40.8	46.9
2μm-53μm	41.0	48.1	46.4	43.2
larger than 53 μm	14.7	18.5	13.5	10.8
sum	99.8	101.0	100.7	100.9
		H_2O_2 control		
less than 2μm	42.6	45.0	43.5	48.2
2μm-53 μm	44.0	35.5	41.6	42.2
larger than 53 μm	13.5	18.9	13.8	10.5
sum	100.1	99.4	98.9	100.9

APPENDIX II (Continued)

Change of Particle Size Distribution Upon Various Drying Treatments

Particle Size	Wet	Oven	P_2O_5	Freeze
		Synthesized Minerals		
		Fe hydrous oxide (A)		
less than 2 μm	100.0	50.0	68.8	82.6
2.0 μm - 53 μm	1.7	20.1	4.9	13.4
larger than 53 μm	0.7	28.8	28.1	3.8
sum	102.4	98.8	101.8	99.8
		Fe hydrous oxide (B)		
less than 2 μm	100.0	93.5	100.0	100.0
2.0 μm - 53 μm	2.7	2.7	2.6	1.1
larger than 53 μm	0	5.9	1.0	2.3
sum	102.7	102.1	103.6	103.4
		Gibbsite/bayerite		
less than 2 μm	88.62	82.00	78.64	86.34
2.0 μm - 53 μm	8.99	13.00	17.94	9.65
larger than 53 μm	2.59	4.83	3.42	4.01
sum	100.0	99.83	100.0	100.0

APPENDIX III

Colloidal Stability
(Particle Size Distribution at Selected pH Values)

0.1N-HCl or NaOH added amounts (ml)	pH	Particle Size Distribution (%)		
		>53 μm	2-53 μm	<2 μm
		Akaka Soil (original)		
56.0	1.85	16.0	75.0	11.0
26.0	2.50	16.0	78.0	7.0
14.0	3.20	17.0	84.0	1.5
7.0	3.60	26.2	75.0	0
3.5	3.90	27.2	74.5	0
1.0	4.40	27.8	74.5	0
0	5.20	27.4	75.0	0
1.0	6.10	28.1	45.9	32.5
3.0	7.00	28.3	45.5	46.3
8.0	8.15	28.0	45.5	4.9
16.0	9.25	27.7	46.8	50.5

APPENDIX III (Continued)

Colloidal Stability
(Particle Size Distribution at Selected pH Values)

0.1N-HCl or NaOH added amounts (ml)	pH	Particle Size Distribution (%)		
		>53μ m	2-53 μm	<2μm
		Hilo Soil (original)		
3.0	3.43	20.1	13.1	66.8
2.5	3.50	22.1	12.0	65.8
2.0	3.77	21.6	12.2	66.2
1.5	4.15	19.6	13.4	67.0
0	5.46	20.1	19.4	60.5
0.4	6.34	23.4	76.6	0
1.0	6.66	20.8	77.2	0
1.4	7.03	23.5	76.5	0
2.5	7.91	24.2	75.8	0
6.0	9.40	24.4	29.4	46.2
10.0	10.25	21.9	21.6	56.5
15.0	10.61	23.2	22.4	54.4
22.0	10.70	21.2	24.8	54.2

APPENDIX III (Continued)

Colloidal Stability
(Particle Size Distribution at Selected pH Values)

0.1N-HCl or NaOH added amounts (ml)	pH	Particle Size Distribution (%)		
		>53μm	2-53μm	<2μm
		Kawaihae Soil (original)		
90.0	1.70	10.8	89.0	0
20.0	2.70	11.0	88.0	0
10.0	2.80	11.8	88.0	0
5.0	3.45	11.4	89.0	0
2.5	4.30	12.3	89.0	0
0.8	5.80	12.8	88.5	0
0.2	6.70	11.7	80.0	8.0
0	7.05	11.5	44.5	43.5
0.8	9.75	11.0	38.5	50.0
1.5	9.50	11.3	38.5	50.0
4.0	10.50	8.8	39.0	52.0
8.0	11.00	8.4	38.0	54.0

APPENDIX III (Continued)

Colloidal Stability
(Particle Size Distribution at Selected pH Values)

0.1N-HCl or NaOH added amounts (ml/l)	pH	Particle Size Distribution (%)		
		>53μm	2-53μm	<2 μm
	Akaka Soil (P_2O_5 dried)			
24.0	2.75	15.1	83.6	0
10.0	4.30	19.6	79.3	0
5.0	4.40	27.5	73.5	0
2.5	4.55	30.6	68.0	0
1.2	4.70	34.8	63.3	0
0.5	4.90	35.9	63.6	0
0	5.15	42.6	56.8	0
0.5	6.60	40.8	42.1	17.1
1.5	7.25	39.0	42.7	18.4
2.5	8.50	40.0	39.0	21.0
5.0	9.70	35.9	24.6	39.5

APPENDIX III (Continued)

Colloidal Stability
(Particle Size Distribution at Selected pH Values)

0.1N-HCl or NaOH added amounts (ml/l)	pH	Particle Size Distribution (%)		
		>53 µm	2-53 µm	<2 µm
		Hilo Soil (P_2O_5 dried)		
19.0	2.40	16.7	25.8	56.2
5.0	4.00	21.7	25.4	51.6
0	5.55	41.2	26.6	31.8
0.5	6.65	38.9	64.6	0
1.0	7.10	38.2	64.2	0
1.5	7.35	38.6	65.4	0
2.0	7.80	41.8	59.3	0
2.5	8.00	35.8	63.8	0
3.5	8.90	34.1	39.0	31.8
5.0	10.20	34.5	25.5	41.3
10.0	11.15	32.4	7.0	60.5

APPENDIX III (Continued)

Colloidal Stability
(Particle Size Distribution at Selected pH Values)

0.1N-HCl or NaOH added amounts (ml/l)	pH	Particle Size Distribution (%)		
		>53μm	2-53μm	<2μm
	Kawaihae Soil (P_2O_5 dried)			
30.0	2.40	10.2	91.5	0
15.0	2.75	11.9	90.0	0
7.0	3.10	9.4	90.0	0
2.5	3.66	10.7	91.0	0
1.0	4.65	13.7	90.5	0
0.5	5.70	11.1	91.5	0
0	7.10	12.7	47.9	40.6
0.8	8.75	10.7	42.2	45.5
1.5	9.60	13.8	42.0	44.0
4.0	10.16	10.2	43.0	45.6
8.0	10.86	10.0	40.0	50.0

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